



Europäisches Patentamt

European Patent Office

Office européen des brevets



(19)

(11)

EP 0 827 027 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
04.03.1998 Bulletin 1998/10

(51) Int Cl. 6: G03F 7/038

(21) Application number: 97306198.9

(22) Date of filing: 15.08.1997

(84) Designated Contracting States:  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE

(30) Priority: 29.08.1996 US 705375

(71) Applicant: XEROX CORPORATION  
Rochester New York 14644 (US)

(72) Inventors:

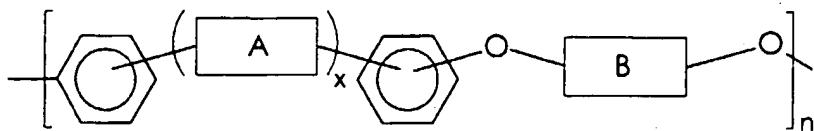
- Narang, Ram S.  
Fairport, NY 14450 (US)
- Fuller, Timothy J.  
Pittsford, NY 14534-4023 (US)

- Smith, Thomas W.  
Penfield, NY 14526 (US)
- Luca, David J.  
Rochester, NY 14609 (US)
- Mosher, Ralph A.  
Rochester, NY 14620 (US)

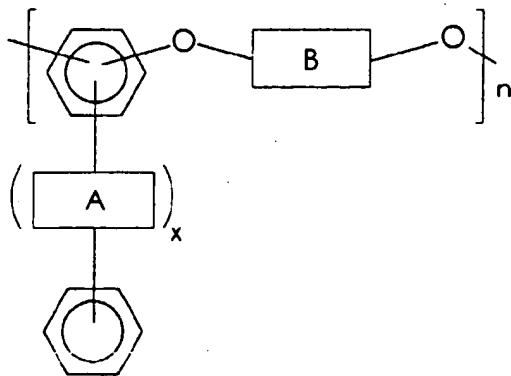
(74) Representative: Pike, Christopher Gerard et al  
Rank Xerox Ltd.,  
Patent Department,  
Parkway  
Marlow, Buckinghamshire SL7 1YL (GB)

### (54) Curable compositions

(57) Disclosed is an improved composition comprising a photopatternable polymer containing at least some monomer repeat units with photosensitivity-imparting substituents, said photopatternable polymer being of the general formula



or



wherein x is an integer of 0 or 1, and A and B are specified groups.

Also disclosed is a process for preparing a thermal ink jet printhead with the aforementioned polymer and a thermal

EP 0 827 027 A2

**EP 0 827 027 A2**

ink jet printhead containing therein a layer of a crosslinked or chain extended polymer of the above formula.

**Description**

The present invention is directed to curable compositions having improved characteristics. The present invention is also directed to improved photoresist compositions and to improved thermal ink jet printheads.

In microelectronics applications, there is a great need for low dielectric constant, high glass transition temperature, thermally stable, photopatternable polymers for use as interlayer dielectric layers and as passivation layers which protect microelectronic circuitry. Poly(imides) are widely used to satisfy these needs; these materials, however, have disadvantageous characteristics such as relatively high water sorption and hydrolytic instability. There is thus a need for high performance polymers which can be effectively photopatterned and developed at high resolution.

One particular application for such materials is the fabrication of ink jet printheads for use in ink jet printing.

Other microelectronics applications include printed circuit boards, lithographic printing processes, and interlayer dielectrics.

Copending application U.S. Serial No. 08/705,365 discloses a composition which comprises a polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation.

Copending application U.S. Serial No. 08/705,488 discloses a composition comprising a polymer with a weight average molecular weight of from about 1,000 to about 65,000, said polymer containing at least some monomer repeat units with a first, photosensitivity-imparting substituent which enables crosslinking or chain extension of the polymer upon exposure to actinic radiation.

Copending application U.S. Serial No. 08/697,761 discloses a process which comprises reacting a defined polymer with (i) a formaldehyde source, and (ii) an unsaturated acid in the presence of an acid catalyst, thereby forming a curable polymer with unsaturated ester groups.

Copending application U.S. Serial No. 08/705,463 discloses a process which comprises reacting a defined polymer with an acetyl halide and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst and methanol, thereby forming a haloalkylated polymer.

Copending application U.S. Serial No. 08/705,479 discloses a process which comprises reacting a haloalkylated aromatic polymer with a material selected from the group consisting of unsaturated ester salts, alkoxide salts, alkyl-carboxylate salts, and mixtures thereof, thereby forming a curable polymer having functional groups corresponding to the selected salt.

Copending application U.S. Serial No. 08/705,376 discloses a composition which comprises a mixture of (A) a first component comprising a polymer, at least some of the monomer repeat units of which have at least one photosensitivity-imparting group thereon, and (B) a second component which comprises either (1) a polymer having a second degree of photosensitivity-imparting group substitution, or (2) a reactive diluent having at least one photosensitivity-imparting group per molecule and having a fourth degree of photosensitivity-imparting group substitution.

Copending application U.S. Serial No. 08/705,372 discloses a composition which comprises a polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation.

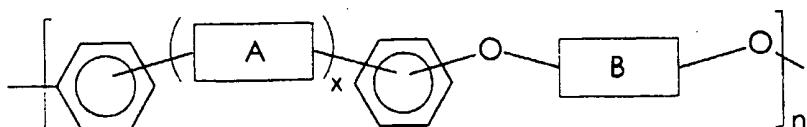
Copending application U.S. Serial No. 08/697,760 discloses a composition which comprises a polymer containing at least some monomer repeat units with water-solubility-imparting substituents and at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation.

While known compositions and processes are suitable for their intended purposes, a need remains for improved materials suitable for microelectronics applications. A need also remains for improved ink jet printheads. Further, there is a need for photopatternable polymeric materials which are heat stable, electrically insulating, and mechanically robust. Additionally, there is a need for photopatternable polymeric materials which are chemically inert with respect to the materials that might be employed in ink jet ink compositions. There is also a need for photopatternable polymeric materials which exhibit low shrinkage during post-cure steps in microelectronic device fabrication processes. In addition, a need remains for photopatternable polymeric materials which exhibit a relatively long shelf life. Further, there is a need for photopatternable polymeric materials which can be patterned with relatively low photo-exposure energies. Additionally, a need remains for photopatternable polymeric materials which, in the cured form, exhibit good solvent resistance. There is also a need for photopatternable polymeric materials which, when applied to microelectronic devices by spin casting techniques and cured, exhibit reduced edge bead and no apparent lips and dips. In addition, there remains a need for photopatternable polymeric materials which have relatively low dielectric constants. Further, there is a need for photopatternable polymeric materials which exhibit reduced water sorption. Additionally, a need remains for photopatternable polymeric materials which exhibit improved hydrolytic stability, especially upon exposure to alkaline solutions. A need also remains for photopatternable polymeric materials which are stable at high temperatures, typically greater than about 150°C. There is also a need for photopatternable polymeric materials which either have high glass transition temperatures or are sufficiently crosslinked that there are no low temperature phase transi-

5 tions subsequent to photoexposure. Further, a need remains for photopatternable polymeric materials with low coefficients of thermal expansion. There is a need for polymers which are thermally stable, patternable as thick films of about 30 microns or more, exhibit low  $T_g$  prior to photoexposure, have low dielectric constants, are low in water absorption, have low coefficients of expansion, have desirable mechanical and adhesive characteristics, and are generally desirable for interlayer dielectric applications, including those at high temperatures, which are also photopatternable. There is also a need for photoresist compositions with good to excellent processing characteristics.

10 According to one aspect of the present invention, there is provided a composition comprising a polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation, said polymer being of the formula

15

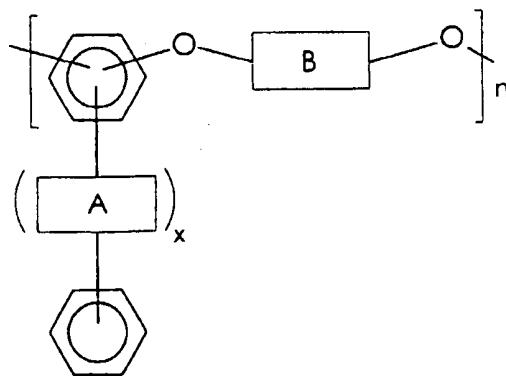


15

or

20

25

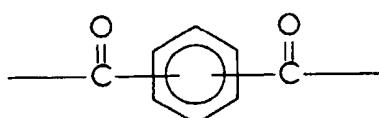


30

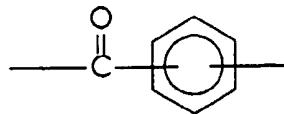
35

wherein  $x$  is an integer of 0 or 1, A is

40



45

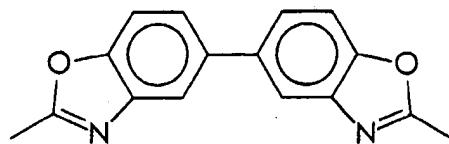


50

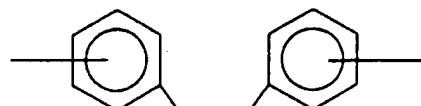


55

5



10



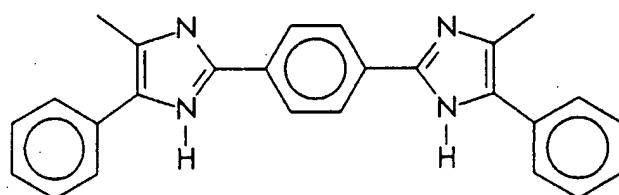
15



20



25



30

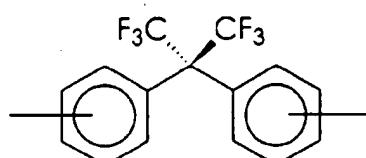
35

-O-,

-C(CH<sub>3</sub>)<sub>2</sub>-

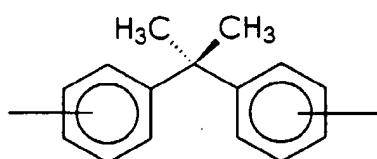
40 or mixtures thereof, B is

45

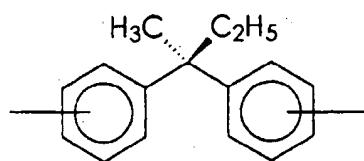


50

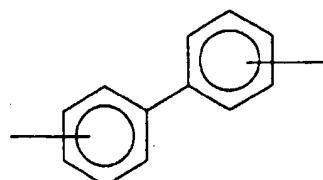
55



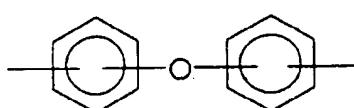
5



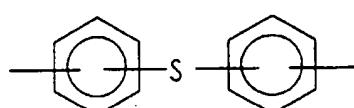
10



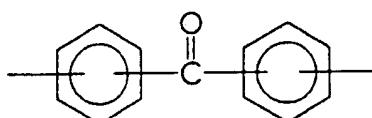
15



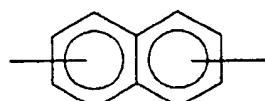
20



30

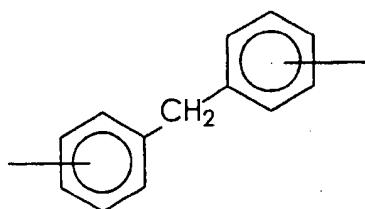


35



40

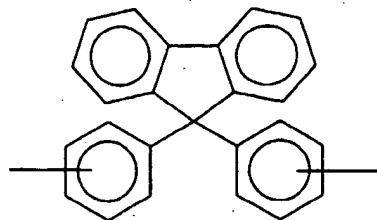
45



50

55

5



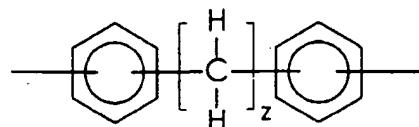
10



15

wherein v is an integer of from 1 to about 20,

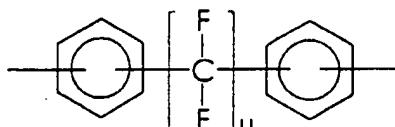
20



25

wherein z is an integer of from 2 to about 20,

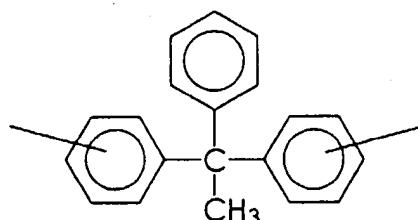
30



35

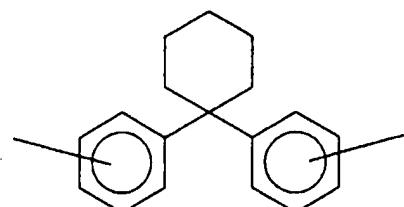
wherein u is an integer of from 1 to about 20,

40

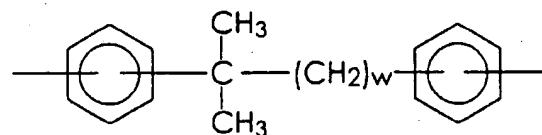
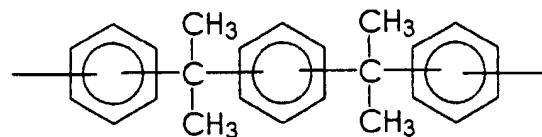


45

50

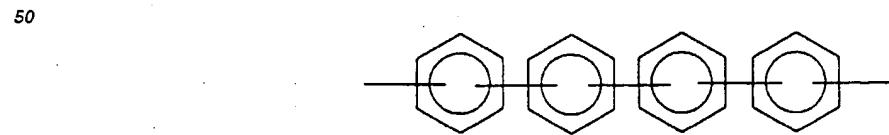
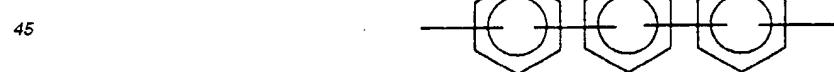
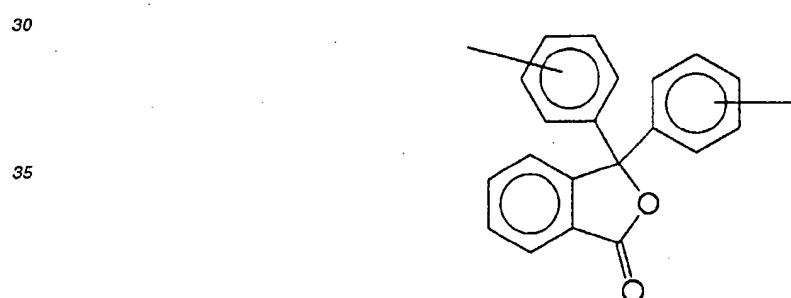
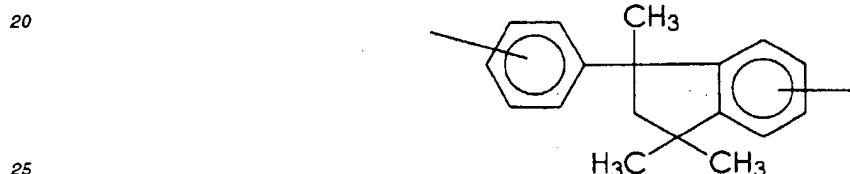


55



15

wherein w is an integer of from 1 to about 20,

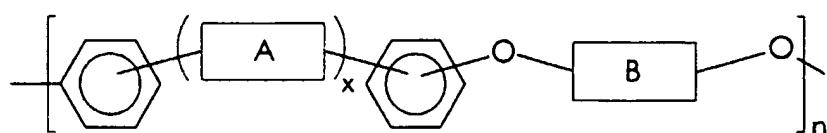


or mixtures thereof, and n is an integer representing the number of repeating monomer units.

According to another aspect of the present invention, there is provided a composition which comprises a crosslinked

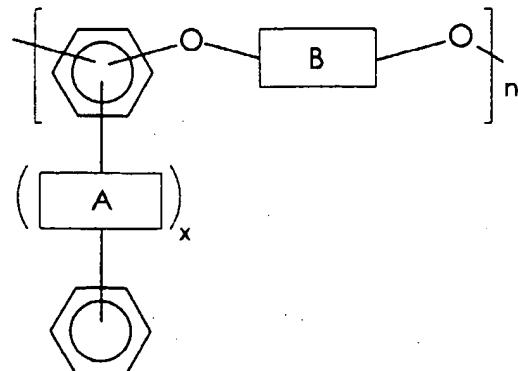
or chain extended polymer of the formula

5



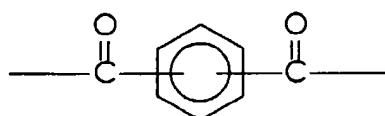
10 or

15



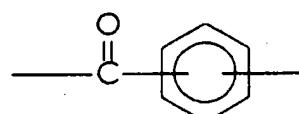
wherein x is an integer of 0 or 1, A is

30

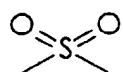


35

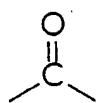
40



45

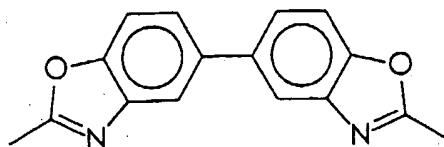


50



55

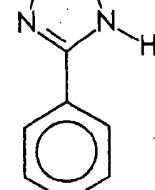
5



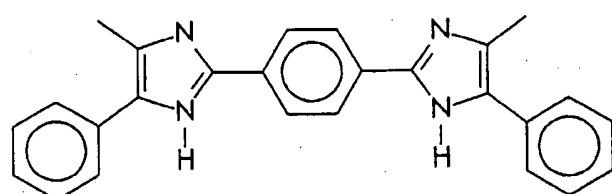
10



15



20



25

30

-O-,

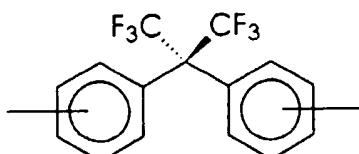
35

-C(CH<sub>3</sub>)<sub>2</sub>,

or mixtures thereof, B is

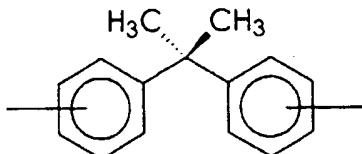
40

45

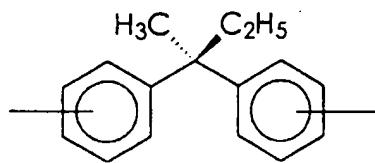


50

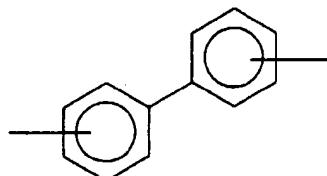
55



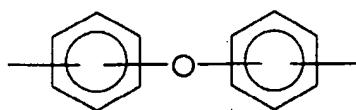
5



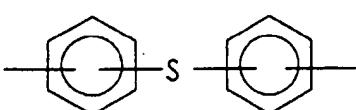
10



15

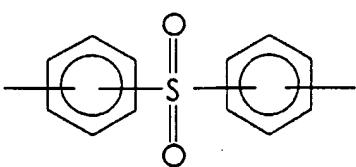


20



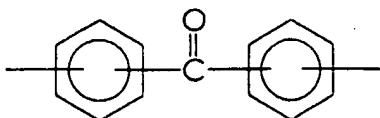
25

30



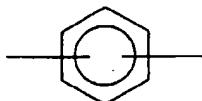
35

40

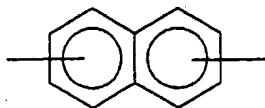


45

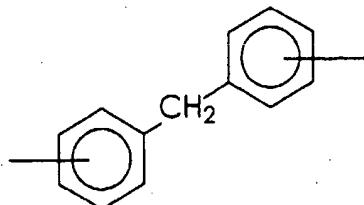
50



55

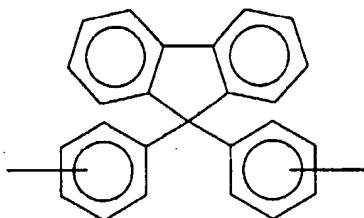


5



10

15



20

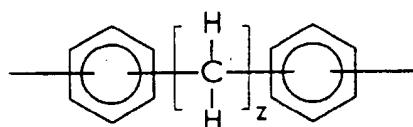
25



30

wherein v is an integer of from 1 to about 20,

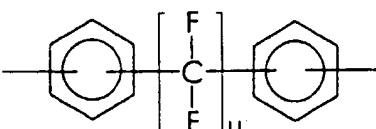
35



40

wherein z is an integer of from 2 to about 20,

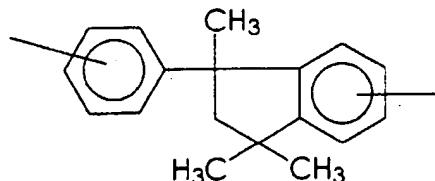
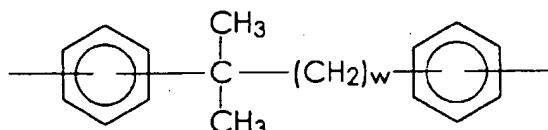
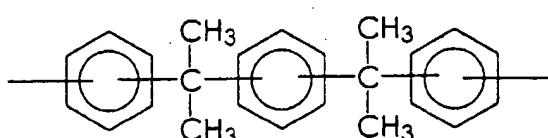
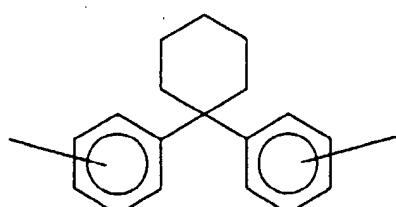
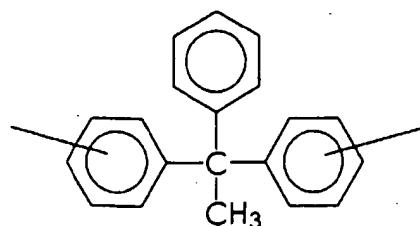
45



50

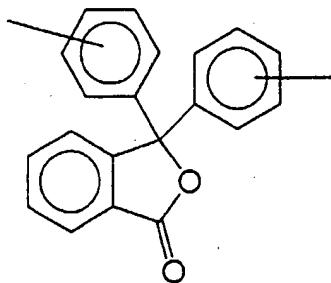
wherein u is an integer of from 1 to about 20,

55



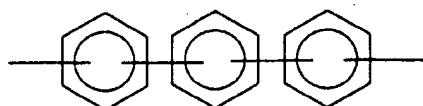
55

5



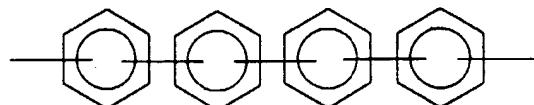
10

15



20

25



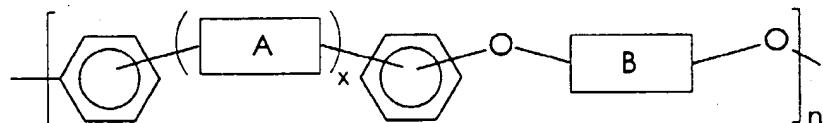
or mixtures thereof, and n is an integer representing the number of repeating monomer units, said crosslinking or chain extension occurring through photosensitivity-imparting substituents contained on at least some of the monomer repeat units of the polymer which form crosslinks or chain extensions in the polymer upon exposure to actinic radiation.

30 According to another aspect of the present invention, there is provided a process which comprises the steps of

(a) providing a polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation, said polymer being of the formula

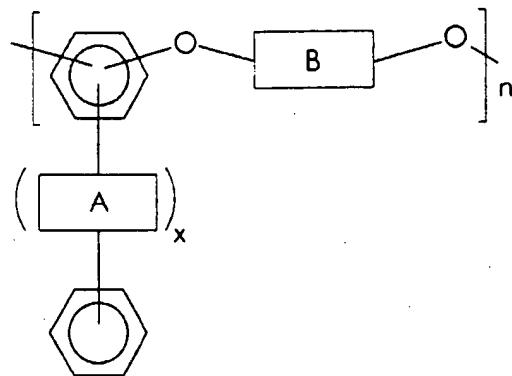
35

40



or

45

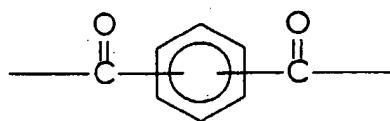


50

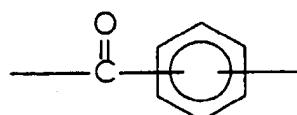
55

wherein x is an integer of 0 or 1, A is

5

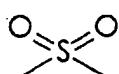


10



15

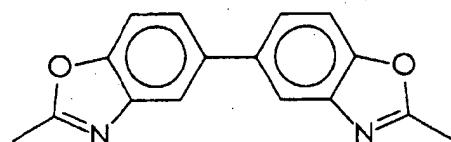
20



25

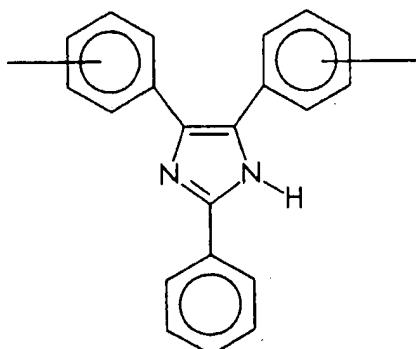


30



35

40

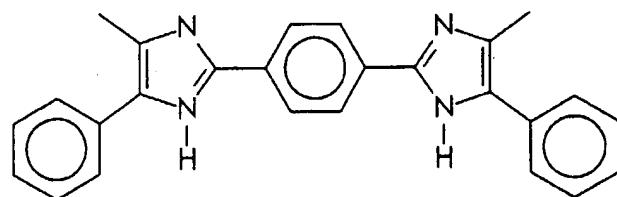


45

50

55

5



10

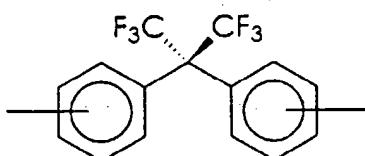
-O-,

15

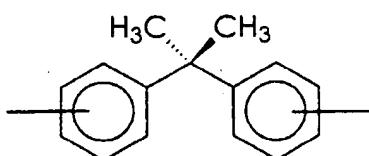
-C(CH<sub>3</sub>)<sub>2</sub>-

or mixtures thereof, B is

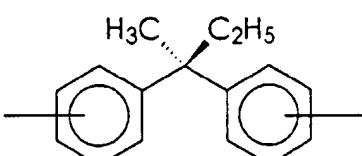
20



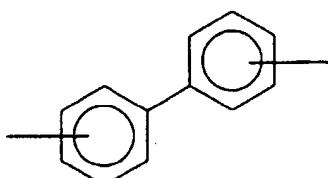
25



35



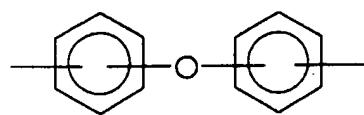
45



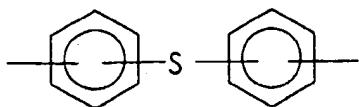
50

55

5

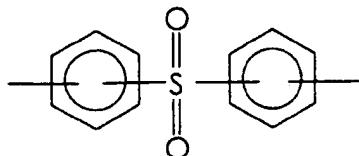


10



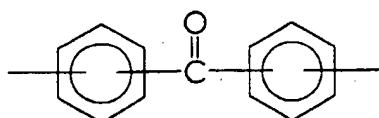
15

20

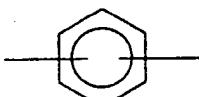


25

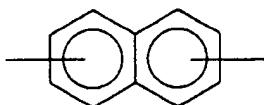
30



35

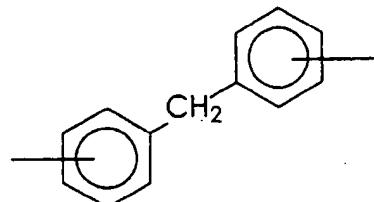


40



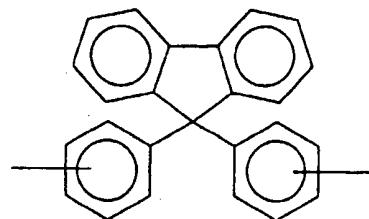
45

50



55

5



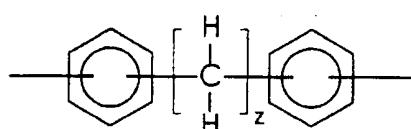
10



15

wherein v is an integer of from 1 to about 20,

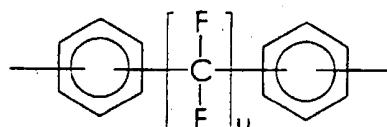
20



25

wherein z is an integer of from 2 to about 20,

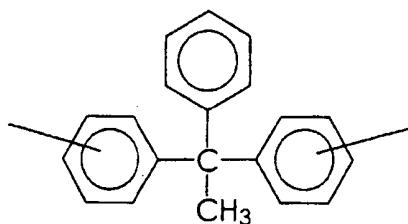
30



35

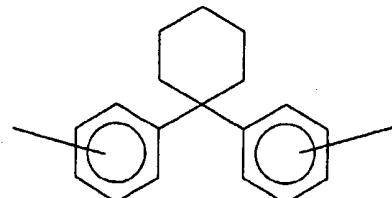
wherein u is an integer of from 1 to about 20,

40



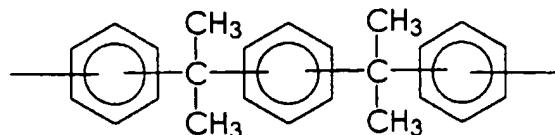
45

50

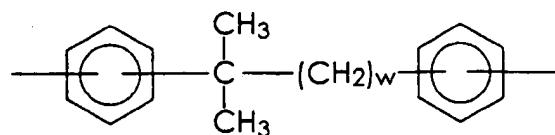


55

5



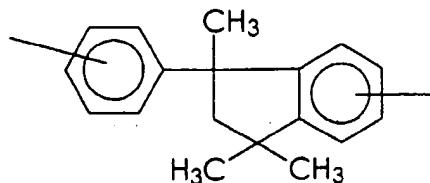
10



15

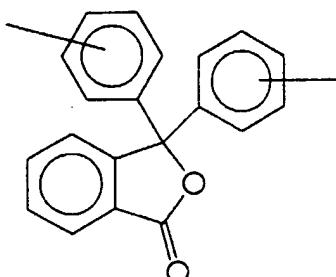
wherein w is an integer of from 1 to about 20,

20



25

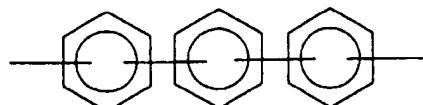
30



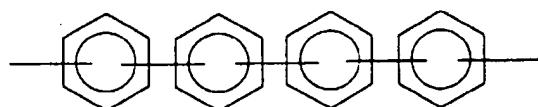
35

40

45



50



55

or mixtures thereof, and n is an integer representing the number of repeating monomer units, and (b) causing the polymer to become crosslinked or chain extended through the photosensitivity-imparting groups.

Figure 1 is an enlarged schematic isometric view of an example of a printhead mounted on a daughter board showing the droplet emitting nozzles.

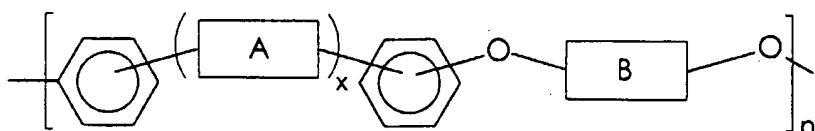
Figure 2 is an enlarged cross-sectional view of Figure 1 as viewed along the line 2-2 thereof and showing the electrode passivation and ink flow path between the manifold and the ink channels.

5 Figure 3 is an enlarged cross-sectional view of an alternate embodiment of the printhead in Figure 1 as viewed along the line 2-2 thereof.

The present invention is directed to an improved composition comprising a photopatternable polymer. Examples of suitable polymers include poly(arylene ether ketones), poly(arylene ethers), poly(arylene ether sulfones), poly(arylene ether heterocyclics), and the like. The photopatternable polymer is of the following formula:

10

15

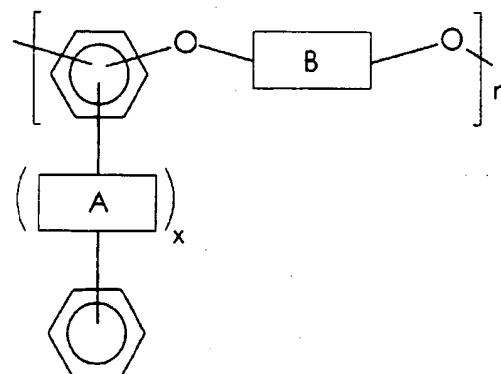


or

20

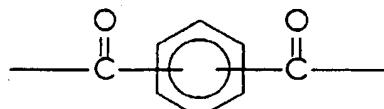
25

30



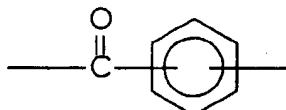
35 wherein x is an integer of 0 or 1, A is

40

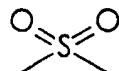


45

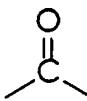
50



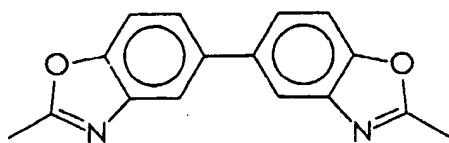
55



5

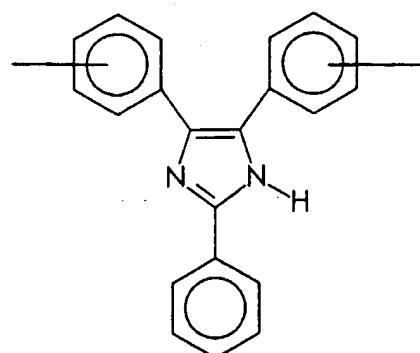


10



15

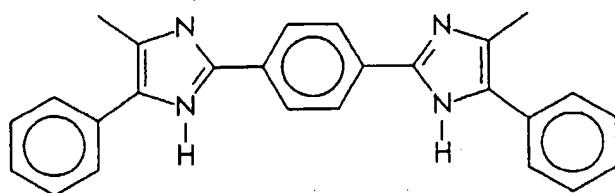
20



25

30

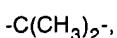
35



40



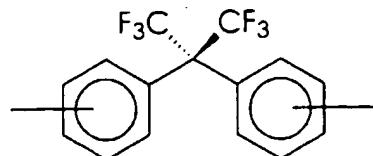
45



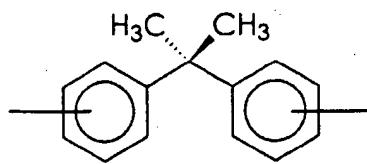
or mixtures thereof, B is

50

55

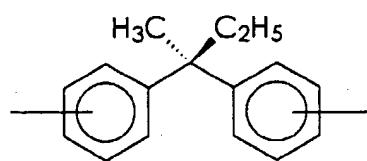


5



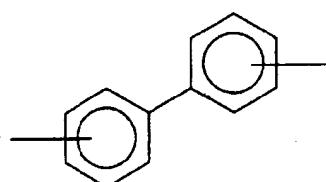
10

15

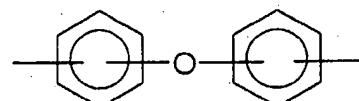


20

25



30



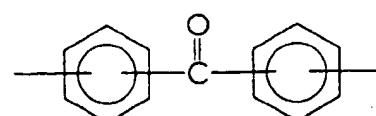
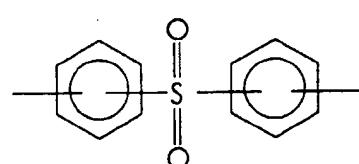
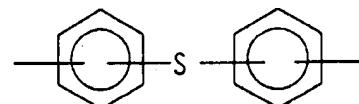
35

40

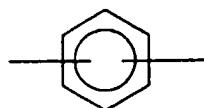
45

50

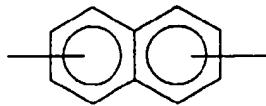
55



5

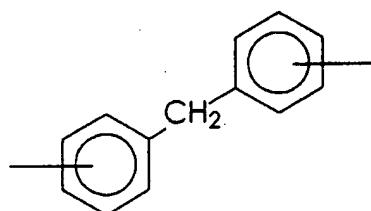


10



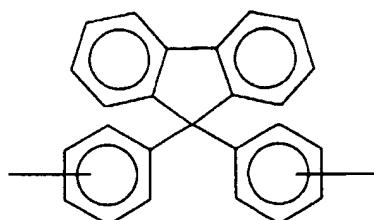
15

20



25

30

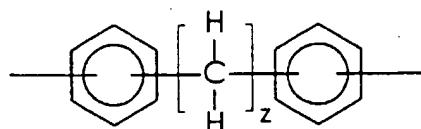


35



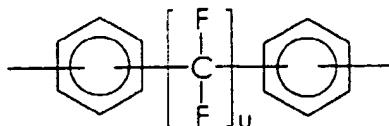
40 wherein  $v$  is an integer of from 1 to about 20, and preferably from 1 to about 10,

45



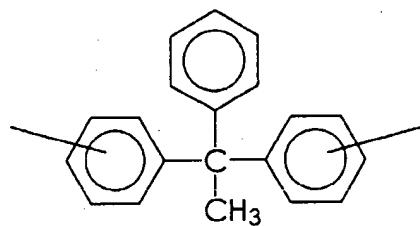
50 wherein  $z$  is an integer of from 2 to about 20, and preferably from 2 to about 10,

55



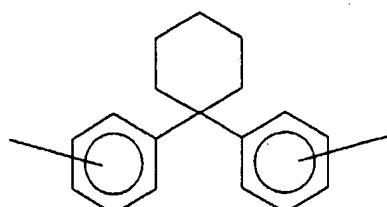
wherein  $u$  is an integer of from 1 to about 20, and preferably from 1 to about 10,

5



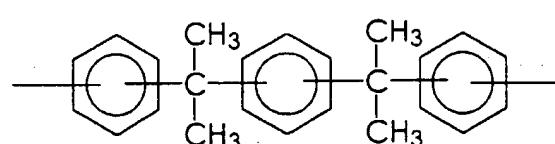
10

15



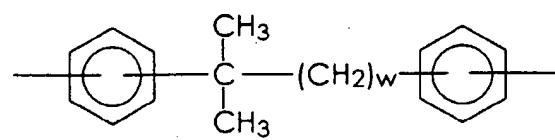
20

25



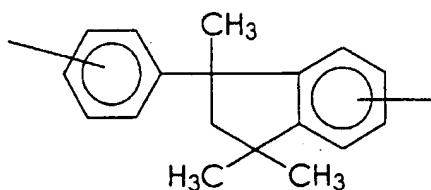
30

35



40 wherein  $w$  is an integer of from 1 to about 20, and preferably from 1 to about 10,

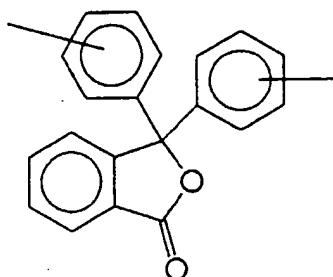
45



50

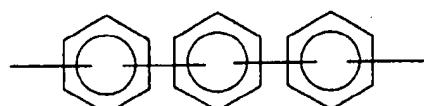
55

5

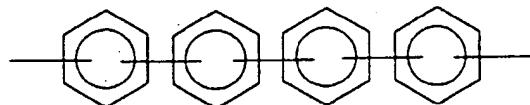


10

15



20



25

other similar bisphenol derivatives, or mixtures thereof, and n is an integer representing the number of repeating monomer units. The value of n is such that the weight average molecular weight of the material is from about 1,000 to about 30 100,000, preferably from about 1,000 to about 65,000, more preferably from about 1,000 to about 40,000, and even more preferably from about 3,000 to about 25,000, although the weight average molecular weight can be outside these ranges. Preferably, n is an integer of from about 2 to about 70, more preferably from about 5 to about 70, and even more preferably from about 8 to about 50, although the value of n can be outside these ranges. The phenyl groups and the A and/or B groups may also be substituted, although the presence of two or more substituents on the B group 35 ortho to the oxygen groups can render substitution difficult. Substituents can be present on the polymer either prior to or subsequent to the placement of photosensitivity-imparting functional groups thereon. Substituents can also be placed on the polymer during the process of placement of photosensitivity-imparting functional groups thereon. Examples of suitable substituents include (but are not limited to) alkyl groups, including saturated, unsaturated, and cyclic alkyl groups, preferably with from 1 to about 6 carbon atoms, substituted alkyl groups, including saturated, unsaturated, and 40 cyclic substituted alkyl groups, preferably with from 1 to about 6 carbon atoms, aryl groups, preferably with from 6 to about 24 carbon atoms, substituted aryl groups, preferably with from 6 to about 24 carbon atoms, arylalkyl groups, preferably with from 7 to about 30 carbon atoms, substituted arylalkyl groups, preferably with from 7 to about 30 carbon atoms, alkoxy groups, preferably with from 1 to about 6 carbon atoms, substituted alkoxy groups, preferably with from 1 to about 6 carbon atoms, aryloxy groups, preferably with from 6 to about 24 carbon atoms, substituted aryloxy groups, 45 preferably with from 6 to about 24 carbon atoms, arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, substituted arylalkyloxy groups, preferably with from 7 to about 30 carbon atoms, hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, ester groups, amide groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, mercapto groups, nitroso groups, sulfone groups, acyl groups, acid anhydride 50 groups, and azide groups, wherein two or more substituents can be joined together to form a ring, wherein the substituents on the substituted alkyl groups, substituted aryl groups, substituted arylalkyl groups, substituted alkoxy groups, substituted aryloxy groups, and substituted arylalkyloxy groups can be (but are not limited to) hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, cyano groups, nitrile groups, mercapto groups, nitroso groups, halogen atoms, nitro groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, mixtures thereof, and the like, wherein two or more substituents can be joined together 55 to form a ring.

The photopatternable polymers of the present invention contain in at least some of the monomer repeat units thereof photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation. Radiation which activates crosslinking or chain extension (actinic radiation) can be of any desired source and any desired wavelength, including (but not limited to) visible light, infrared light, ultraviolet light, 5 electron beam radiation, x-ray radiation, or the like. Examples of suitable photosensitivity imparting groups include unsaturated ester groups, such as acryloyl groups, methacryloyl groups, cinnamoyl groups, crotonoyl groups, ethacryloyl groups, oleoyl groups, linoleoyl groups, maleoyl groups, fumaroyl groups, itaconoyl groups, citraconoyl groups, phenylmaleoyl groups, esters of 3-hexene-1,6-dicarboxylic acid, and the like. Also suitable are alkylcarboxymethylene and ether groups. Under certain conditions, such as imaging with electron beam, deep ultraviolet, or x-ray radiation, 10 halomethyl groups are also photoactive. Epoxy groups, allyl ether groups, hydroxyalkyl groups, and unsaturated ammonium, phosphonium, and ether groups are also suitable photoactive groups.

The photopatternable polymers containing these groups can be prepared by any suitable or desired process. For example, the desired functional group or groups can be applied directly to the polymer. Alternatively, one or more intermediate materials can be prepared. For example, the polymer backbone can be functionalized with a substituent 15 which allows for the facile derivatization of the polymer backbone, such as hydroxyl groups, carboxyl groups, haloalkyl groups such as chloromethyl groups, hydroxyalkyl groups such as hydroxy methyl groups, methoxy methyl groups, and alkylcarboxymethylene groups.

Unsaturated ester groups can be placed on the polymer backbone by any suitable or desired process including 20 those described in copending U.S. Serial No. 08/697,761. For example, substitution of the polymer can be accomplished by reacting the polymer in solution with (a) the appropriate unsaturated acid (such as acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, ethacrylic acid, oleic acid, linoleic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, 3-hexene-1,6-dicarboxylic acid), and (b) a formaldehyde source (i.e., either formaldehyde or a material which, under the conditions of the reaction, generates formaldehyde; examples of formaldehyde sources in addition to formaldehyde include paraformaldehyde, trioxane, methylal, dimethoxymethane, and the like). 25 The reaction is direct acid catalyzed; the polymer is dissolved in a suitable solvent and is allowed to react with the formaldehyde source at about 105°C in the presence of catalytic amounts of para-toluenesulfonic acid. Examples of solvents suitable for the reaction include 1,1,2,2-tetrachloroethane and, if a suitable pressure reactor is used, methylene chloride. Typically, the reactants are present in relative amounts with respect to each other (by weight) of about 10 30 parts polymer, about 5 parts formaldehyde source, about 1 part para-toluenesulfonic acid, about 15.8 parts of the appropriate acid (e.g., acrylic acid, methacrylic acid), about 0.2 parts hydroquinone methyl ether, and about 162 parts 1,1,2,2-tetrachloroethane.

The polymers of the above general formula can also be substituted with photosensitivity-imparting groups such 35 as unsaturated ester groups by first preparing the haloalkylated derivative and then replacing at least some of the haloalkyl groups with unsaturated ester groups as, for example, described in copending U.S. Serial No. 08/705,479.

For example, the haloalkylated polymer can be substituted with unsaturated ester groups by reacting the 40 haloalkylated polymer with an unsaturated ester salt in solution. Examples of suitable reactants include selected salts of Groups IA, IIB, IIIB, IVB, VB, VIB, VIIIB, IB, IIB, IIIA, IVA, of the periodic table with the appropriate unsaturated ester, such as the ester salts of acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, ethacrylic acid, oleic acid, linoleic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, 3-hexene-1,6-dicarboxylic acid, and the like, with specific examples including sodium, potassium, quaternary ammonium, phosphonium, and the like 45 salts of acrylate, methacrylate, cinnamate, and the like. Examples of solvents suitable for the reaction include polar aprotic solvents such as N,N-dimethylacetamide, dimethylsulfoxide, N-methylpyrrolidinone, and dimethylformamide. Typically, the reactants are present in relative amounts with respect to each other by weight of about 10 parts haloalkylated polymer, about 66.5 parts solvent, and about 5.7 parts unsaturated ester salt.

The haloalkylated polymer can be allyl ether substituted or epoxidized by first reacting the haloalkylated polymer 50 with an unsaturated alcohol salt, such as an allyl alcohol salt, in solution as, for example, described in U.S. Serial No. 08/705,372. Examples of suitable unsaturated alcohol salts and allyl alcohol salts include sodium 2-allylphenolate, sodium 4-allylphenolate, sodium allyl alcoholate, corresponding salts with lithium, potassium, cesium, rubidium, ammonium, quaternary alkyl ammonium compounds, and the like. Unsaturated alcohol salts can be generated by the reaction of the alcohol with a base, such as sodium hydride, sodium hydroxide, or the like. The salt displaces the halide of the haloalkyl groups at between about 25 and about 100°C. Examples of solvents suitable for the reaction include polar aprotic solvents such as N,N-dimethylacetamide, dimethylsulfoxide, N-methylpyrrolidinone, dimethylformamide, tetrahydrofuran, and the like. Typically, the reactants are present in relative amounts with respect to each other of from about 1 to about 50 molar equivalents of unsaturated alcohol salt per haloalkyl group to be substituted, although the relative amounts can be outside this range. Typically, the reactants are present in solution in amounts of from about 5 to about 50 percent by weight solids, and preferably about 10 percent by weight solids, although the relative amounts 55 can be outside this range.

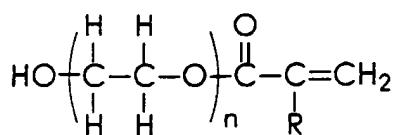
Haloalkylated polymer can be substituted with a photosensitivity-imparting, water-solubility-enhancing (or water-

dispersability-enhancing) group by reacting the haloalkylated polymer with an unsaturated amine, phosphine, or alcohol, as, for example, described in U.S. Serial No. 08/697,760.

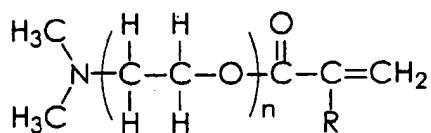
Examples of suitable reactants include N,N-dimethyl ethyl methacrylate, N,N-dimethyl ethyl acrylate,

5

10



15

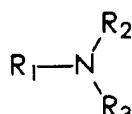


20 wherein R is H or  $\text{CH}_3$  and n is an integer of from 1 to about 50.

In another embodiment, the polymer is substituted with two different functional groups, one of which imparts photosensitivity to the polymer and one of which imparts water solubility or water dispersability to the polymer. Examples of reactants which can be reacted with the polymer to substitute the polymer with suitable water solubility enhancing groups or water dispersability enhancing groups include tertiary amines, of the general formula

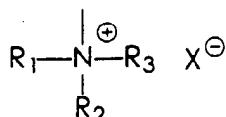
25

30



which add to the polymer quaternary ammonium groups, of the general formula

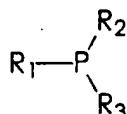
35



40 wherein  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  each, independently of the others, can be (but are not limited to) alkyl groups, typically with from 1 to about 30 carbon atoms, substituted alkyl groups, aryl groups, typically with from 6 to about 18 carbon atoms, substituted aryl groups, arylalkyl groups, typically with from 7 to about 19 carbon atoms, and substituted arylalkyl groups, and X represents a halogen atom, such as fluorine, chlorine, bromine, or iodine; tertiary phosphines, of the general formula

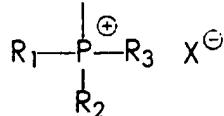
45

50



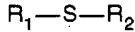
which add to the polymer quaternary phosphonium groups of the general formula

55



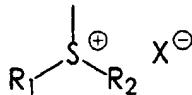
wherein  $R_1$ ,  $R_2$ , and  $R_3$  each, independently of the others, can be (but are not limited to) alkyl groups, typically with from 1 to about 30 carbon atoms, substituted alkyl groups, aryl groups, typically with from 6 to about 18 carbon atoms, substituted aryl groups, arylalkyl groups, typically with from 7 to about 19 carbon atoms, and substituted arylalkyl groups, and  $X$  represents a halogen atom, such as fluorine, chlorine, bromine, or iodine; alkyl thio ethers, of the general formula

5



10 which add to the polymer sulfonium groups of the general formula

15



wherein  $R_1$  and  $R_2$  each, independently of the other, can be (but are not limited to) alkyl groups, typically with from 1 to about 6 carbon atoms and preferably with 1 carbon atom, and substituted alkyl groups, and  $X$  represents a halogen atom, such as fluorine, chlorine, bromine, or iodine; wherein the substituents on the substituted alkyl, aryl, and arylalkyl groups can be (but are not limited to) hydroxy groups, amine groups, imine groups, ammonium groups, pyridine groups, pyridinium groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, cyano groups, nitrile groups, mercapto groups, nitroso groups, halogen atoms, nitro groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, mixtures thereof, and the like, wherein two or more substituents can be joined together to form a ring.

20 The hydroxymethylation of a polymer of the above formula can be accomplished by reacting the polymer in solution with formaldehyde or paraformaldehyde and a base, such as sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, or tetramethylammonium hydroxide as, for example, described in U.S. Serial No. 08/705,365.

25 Polymers of the above formula can also be hydroxyalkylated by first preparing the haloalkylated derivative and then replacing at least some of the haloalkyl groups with hydroxyalkyl groups as, for example, described in U.S. Serial No. 08/705,365.

30 Intermediate derivatives can also be prepared by any suitable or desired process. For example, suitable processes for haloalkylating polymers include reaction of the polymers with formaldehyde and hydrochloric acid, bischloromethyl ether, chloromethyl methyl ether, octylchloromethyl ether, or the like, generally in the presence of a Lewis acid catalyst. 35 Bromination of a methyl group on the polymer can also be accomplished with elemental bromine via a free radical process initiated by, for example, a peroxide initiator or light. Halogen atoms can be substituted for other halogens already on a halomethyl group by, for example, reaction with the appropriate hydrohalic acid or halide salt. Methods 40 for the haloalkylation of polymers are also disclosed in, for example, "Chloromethylation of Condensation Polymers Containing an Oxy-1,4-Phenylene Backbone," W. H. Daly et al., *Polymer Preprints*, Vol. 20, No. 1, 835 (1979).

45 One specific process suitable for haloalkylating the polymer entails reacting the polymer with an acetyl halide, such as acetyl chloride, and dimethoxymethane in the presence of a halogen-containing Lewis acid catalyst, such as those of the general formula

45

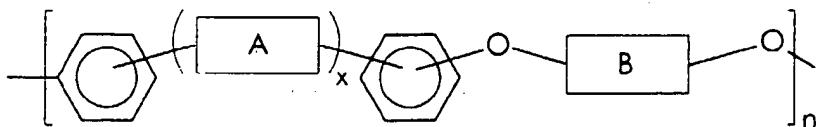


50 wherein  $n$  is an integer of 1, 2, 3, 4, or 5,  $M$  represents a boron atom or a metal atom, such as tin, aluminum, zinc, antimony, iron (III), gallium, indium, arsenic, mercury, copper, platinum, palladium, or the like, and  $X$  represents a halogen atom, such as fluorine, chlorine, bromine, or iodine, with specific examples including  $SnCl_4$ ,  $AlCl_3$ ,  $ZnCl_2$ ,  $AlBr_3$ ,  $BF_3$ ,  $SbF_5$ ,  $FeI_3$ ,  $GaBr_3$ ,  $InCl_3$ ,  $AsI_5$ ,  $HgBr_2$ ,  $CuCl$ ,  $PdCl_2$ , or  $PtBr_2$ . A suitable process is described in U.S. Serial No. 08/705,463.

55 In some instances, the terminal groups on the polymer can be selected by the stoichiometry of the polymer synthesis. For example, when a polymer is prepared by the reaction of 4,4'-dichlorobenzophenone and bis-phenol A in the presence of potassium carbonate in N,N-dimethylacetamide, if the bis-phenol A is present in about 7.5 to 8 mole percent excess, the resulting polymer generally is bis-phenol A-terminated (wherein the bis-phenol A moiety may or may not have one or more hydroxy groups thereon), and the resulting polymer typically has a polydispersity ( $M_w/M_n$ )

of from about 2 to about 3.5. When the bis-phenol A-terminated polymer is subjected to further reactions to place functional groups thereon, such as haloalkyl groups, and/or to convert one kind of functional group, such as a haloalkyl group, to another kind of functional group, such as an unsaturated ester group, the polydispersity of the polymer can rise to the range of from about 4 to about 6. In contrast, if the 4,4'-dichlorobenzophenone is present in about 7.5 to 8 mole percent excess, the reaction time is approximately half that required for the bis-phenol A excess reaction, the resulting polymer generally is benzophenone-terminated (wherein the benzophenone moiety may or may not have one or more chlorine atoms thereon), and the resulting polymer typically has a polydispersity of from about 2 to about 3.5. When the benzophenone-terminated polymer is subjected to further reactions to place functional groups thereon, such as haloalkyl groups, and/or to convert one kind of functional group, such as a haloalkyl group, to another kind of functional group, such as an unsaturated ester group, the polydispersity of the polymer typically remains in the range of from about 2 to about 3.5. Similarly, when a polymer is prepared by the reaction of 4,4'-difluorobenzophenone with either 9,9'-bis(4-hydroxyphenyl)fluorene or bis-phenol A in the presence of potassium carbonate in N,N-dimethylacetamide, if the 4,4'-difluorobenzophenone reactant is present in excess, the resulting polymer generally has benzophenone terminal groups (which may or may not have one or more fluorine atoms thereon). The well-known Carothers equation can be employed to calculate the stoichiometric offset required to obtain the desired molecular weight. (See, for example, William H. Carothers, "An Introduction to the General Theory of Condensation Polymers," *Chem. Rev.*, **8**, 353 (1931) and *J. Amer. Chem. Soc.*, **51**, 2548 (1929); see also P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953). More generally speaking, during the preparation of polymers of the formula

20



25

the stoichiometry of the polymer synthesis reaction can be adjusted so that the end groups of the polymer are derived from the "A" groups or derived from the "B" groups. Specific functional groups can also be present on these terminal "A" groups or "B" groups, such as ethynyl groups or other thermally sensitive groups, hydroxy groups which are attached to the aromatic ring on an "A" or "B" group to form a phenolic moiety, halogen atoms which are attached to the "A" or "B" group, or the like.

Polymers with end groups derived from the "A" group, such as benzophenone groups or halogenated benzophenone groups, may be preferred for some applications because both the syntheses and some of the reactions of these materials to place substituents thereon may be easier to control and may yield better results with respect to, for example, cost, molecular weight, molecular weight range, and polydispersity ( $M_w/M_n$ ) compared to polymers with end groups derived from the "B" group, such as bis-phenol A groups (having one or more hydroxy groups on the aromatic rings thereof) or other phenolic groups. While not being limited to any particular theory, it is believed that the haloalkylation reaction in particular proceeds most rapidly on the phenolic tails when the polymer is bis-phenol A terminated. Moreover, it is believed that halomethylated groups on phenolic-terminated polymers may be particularly reactive to subsequent crosslinking or chain extension. In contrast, it is generally believed that halomethylation does not take place on the terminal aromatic groups with electron withdrawing substituents, such as benzophenone, halogenated benzophenone, or the like. The "A" group terminated materials may also function as an adhesive, and in applications such as thermal ink jet printheads, the use of the crosslinked "A" group terminated polymer may reduce or eliminate the need for an epoxy adhesive to bond the heater plate to the channel plate.

The photopatternable polymer can be cured by uniform exposure to actinic radiation at wavelengths and/or energy levels capable of causing crosslinking or chain extension of the polymer through the photosensitivity-imparting groups. Alternatively, the photopatternable polymer is developed by imagewise exposure of the material to radiation at a wavelength and/or at an energy level to which the photosensitivity-imparting groups are sensitive. Typically, a photoresist composition will contain the photopatternable polymer, an optional solvent for the photopatternable polymer, an optional sensitizer, and an optional photoinitiator. Solvents may be particularly desirable when the uncrosslinked photopatternable polymer has a high  $T_g$ . The solvent and photopatternable polymer typically are present in relative amounts of from 0 to about 99 percent by weight solvent and from about 1 to 100 percent polymer, preferably are present in relative amounts of from about 20 to about 60 percent by weight solvent and from about 40 to about 80 percent by weight polymer, and more preferably are present in relative amounts of from about 30 to about 60 percent by weight solvent and from about 40 to about 70 percent by weight polymer, although the relative amounts can be outside these ranges.

Sensitizers absorb light energy and facilitate the transfer of energy to unsaturated bonds which can then react to crosslink or chain extend the resin. Sensitizers frequently expand the useful energy wavelength range for photoexposure, and typically are aromatic light absorbing chromophores. Sensitizers can also lead to the formation of photoini-

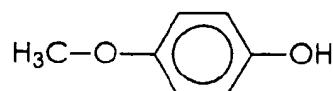
5 initiators, which can be free radical or ionic. When present, the optional sensitizer and the photopatternable polymer typically are present in relative amounts of from about 0.1 to about 20 percent by weight sensitizer and from about 80 to about 99.9 percent by weight photopatternable polymer, and preferably are present in relative amounts of from about 1 to about 10 percent by weight sensitizer and from about 90 to about 99 percent by weight photopatternable polymer, although the relative amounts can be outside these ranges.

10 Photoinitiators generally generate ions or free radicals which initiate polymerization upon exposure to actinic radiation. When present, the optional photoinitiator and the photopatternable polymer typically are present in relative amounts of from about 0.1 to about 20 percent by weight photoinitiator and from about 80 to about 99.9 percent by weight photopatternable polymer, and preferably are present in relative amounts of from about 1 to about 10 percent by weight photoinitiator and from about 90 to about 99 percent by weight photopatternable polymer, although the relative amounts can be outside these ranges.

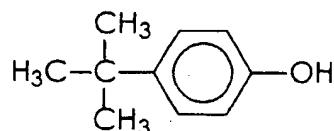
15 A single material can also function as both a sensitizer and a photoinitiator.

20 Examples of specific sensitizers and photoinitiators include Michler's ketone (Aldrich Chemical Co.), Darocure 1173, Darocure 4265, Irgacure 184, Irgacure 261, and Irgacure 907 (available from Ciba-Geigy, Ardsley, New York), and mixtures thereof. Benzophenone and its derivatives can function as photosensitizers. Triphenylsulfonium and diphenyl iodonium salts are examples of typical cationic photoinitiators.

25 Inhibitors may also optionally be present in the photoresist containing the photopatternable polymer. Examples of suitable inhibitors include MEHQ, a methyl ether of hydroquinone, of the formula



25 t-butylcatechol, of the formula



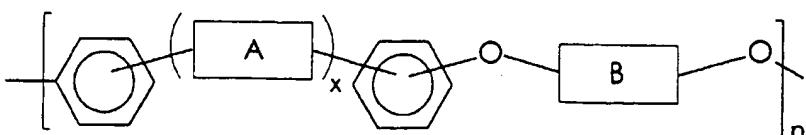
35 hydroquinone, of the formula



45 and the like, the inhibitor typically present in an amount of from about 500 to about 1,500 parts per million by weight of a photoresist solution containing about 40 percent by weight polymer solids, although the amount can be outside this range.

50 Many of the photosensitivity-imparting groups which are indicated above as being capable of enabling crosslinking or chain extension of the polymer upon exposure to actinic radiation can also enable crosslinking or chain extension of the polymer upon exposure to elevated temperatures; thus the polymers of the present invention can also, if desired, be used in applications wherein thermal curing is employed.

55 In all of the above reactions and substitutions illustrated above for the polymer of the formula



it is to be understood that analogous reactions and substitutions will occur for the polymer of the formula

5

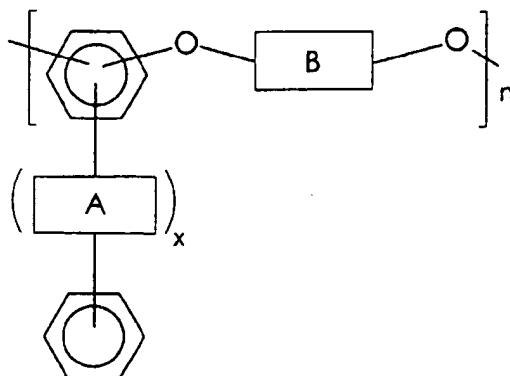
10

15

Photopatternable polymeric materials of the present invention can be used as components in ink jet printheads. The printheads of the present invention can be of any suitable configuration. An example of a suitable configuration, suitable in this instance for thermal ink jet printing, is illustrated schematically in Figure 1, which depicts an enlarged, schematic isometric view of the front face 29 of a printhead 10 showing the array of droplet emitting nozzles 27. Referring also to Figure 2, discussed later, the lower electrically insulating substrate or heating element plate 28 has the heating elements 34 and addressing electrodes 33 patterned on surface 30 thereof, while the upper substrate or channel plate 31 has parallel grooves 20 which extend in one direction and penetrate through the upper substrate front face edge 29. The other end of grooves 20 terminate at slanted wall 21, the floor 41 of the internal recess 24 which is used as the ink supply manifold for the capillary filled ink channels 20, has an opening 25 therethrough for use as an ink fill hole. The surface of the channel plate with the grooves are aligned and bonded to the heater plate 28, so that a respective one of the plurality of heating elements 34 is positioned in each channel, formed by the grooves and the lower substrate or heater plate. Ink enters the manifold formed by the recess 24 and the lower substrate 28 through the fill hole 25 and by capillary action, fills the channels 20 by flowing through an elongated recess 38 formed in the thick film insulative layer 18. The ink at each nozzle forms a meniscus, the surface tension of which prevents the ink from weeping therefrom. The addressing electrodes 33 on the lower substrate or channel plate 28 terminate at terminals 32. The upper substrate or channel plate 31 is smaller than that of the lower substrate in order that the electrode terminals 32 are exposed and available for wire bonding to the electrodes on the daughter board 19, on which the printhead 10 is permanently mounted. Layer 18 is a thick film passivation layer, discussed later, sandwiched between the upper and lower substrates. This layer is etched to expose the heating elements, thus placing them in a pit, and is etched to form the elongated recess to enable ink flow between the manifold 24 and the ink channels 20. In addition, the thick film insulative layer is etched to expose the electrode terminals.

A cross sectional view of Figure 1 is taken along view line 2-2 through one channel and shown as Figure 2 to show how the ink flows from the manifold 24 and around the end 21 of the groove 20 as depicted by arrow 23. As is disclosed in U.S. Patent 4,638,337, U.S. Patent 4,601,777, and U.S. Patent Re. 32,572, a plurality of sets of bubble generating heating elements 34 and their addressing electrodes 33 can be patterned on the polished surface of a single side polished (100) silicon wafer. Prior to patterning, the multiple sets of printhead electrodes 33, the resistive material that serves as the heating elements 34, and the common return 35, the polished surface of the wafer is coated with an underglaze layer 39 such as silicon dioxide, having a typical thickness of from about 5,000 Angstroms to about 2 microns, although the thickness can be outside this range. The resistive material can be a doped polycrystalline silicon, which can be deposited by chemical vapor deposition (CVD) or any other well known resistive material such as zirconium boride ( $ZrB_2$ ). The common return and the addressing electrodes are typically aluminum leads deposited on the underglaze and over the edges of the heating elements. The common return ends or terminals 37 and addressing electrode terminals 32 are positioned at predetermined locations to allow clearance for wire bonding to the electrodes (not shown) of the daughter board 19, after the channel plate 31 is attached to make a printhead. The common return 35 and the addressing electrodes 33 are deposited to a thickness typically of from about 0.5 to about 3 microns, although the thickness can be outside this range, with the preferred thickness being 1.5 microns.

If polysilicon heating elements are used, they may be subsequently oxidized in steam or oxygen at a relatively high temperature, typically about 1,100°C although the temperature can be above or below this value, for a period of time typically of from about 50 to about 80 minutes, although the time period can be outside this range, prior to the deposition of the aluminum leads, in order to convert a small portion of the polysilicon to  $SiO_2$ . In such cases, the heating elements are thermally oxidized to achieve an overglaze (not shown) of  $SiO_2$  with a thickness typically of from about 500 Angstroms to about 1 micron, although the thickness can be outside this range, which has good integrity with substantially no pinholes.



5 In one embodiment, polysilicon heating elements are used and an optional silicon dioxide thermal oxide layer 17 is grown from the polysilicon in high temperature steam. The thermal oxide layer is typically grown to a thickness of from about 0.5 to about 1 micron, although the thickness can be outside this range, to protect and insulate the heating elements from the conductive ink. The thermal oxide is removed at the edges of the polysilicon heating elements for attachment of the addressing electrodes and common return, which are then patterned and deposited. If a resistive material such as zirconium boride is used for the heating elements, then other suitable well known insulative materials can be used for the protective layer thereover. Before electrode passivation, a tantalum (Ta) layer (not shown) can be 10 optionally deposited, typically to a thickness of about 1 micron, although the thickness can be above or below this value, on the heating element protective layer 17 for added protection thereof against the cavitation forces generated by the collapsing ink vapor bubbles during printhead operation. The tantalum layer is etched off all but the protective layer 17 directly over the heating elements using, for example,  $CF_4/O_2$  plasma etching. For polysilicon heating elements, the aluminum common return and addressing electrodes typically are deposited on the underglaze layer and over the opposing edges of the polysilicon heating elements which have been cleared of oxide for the attachment of the common return and electrodes.

15 For electrode passivation, a film 16 is deposited over the entire wafer surface, including the plurality of sets of heating elements and addressing electrodes. The passivation film 16 provides an ion barrier which will protect the exposed electrodes from the ink. Examples of suitable ion barrier materials for passivation film 16 include polyimide, plasma nitride, phosphorous doped silicon dioxide, materials disclosed hereinafter as being suitable for insulative layer 18, and the like, as well as any combinations thereof. An effective ion barrier layer is generally achieved when its 20 thickness is from about 100 nanometers (1000 Angstroms) to about 10 micrometers (microns), although the thickness can be outside this range. In 300 dpi printheads, passivation layer 16 preferably has a thickness of about 3 micrometers (microns), although the thickness can be above or below this value. In 600 dpi printheads, the thickness of passivation layer 16 preferably is such that the combined thickness of layer 16 and layer 18 is about 25 micrometers (microns), although the thickness can be above or below this value. The passivation film or layer 16 is etched off of the terminal 25 ends of the common return and addressing electrodes for wire bonding later with the daughter board electrodes. This etching of the silicon dioxide film can be by either the wet or dry etching method. Alternatively, the electrode passivation can be by plasma deposited silicon nitride ( $Si_3N_4$ ).

30 Next, a thick film type insulative layer 18, of a polymeric material discussed in further detail herein, is formed on the passivation layer 16, typically having a thickness of from about 10 to about 100 micrometers (microns) and preferably in the range of from about 25 to about 50 micrometers (microns), although the thickness can be outside these ranges. Even more preferably, in 300 dpi printheads, layer 18 preferably has a thickness of about 30 micrometers (microns), and in 600 dpi printheads, layer 18 preferably has a thickness of from about 20 to about 22 micrometers (microns), although other thicknesses can be employed. The insulative layer 18 is photolithographically processed to 35 enable etching and removal of those portions of the layer 18 over each heating element (forming recesses 26), the elongated recess 38 for providing ink passage from the manifold 24 to the ink channels 20, and over each electrode terminal 32, 37. The elongated recess 38 is formed by the removal of this portion of the thick film layer 18. Thus, the passivation layer 16 alone protects the electrodes 33 from exposure to the ink in this elongated recess 38. Optionally, if desired, insulative layer 18 can be applied as a series of thin layers of either similar or different composition. Typically, a thin layer is deposited, photoexposed, partially cured, followed by deposition of the next thin layer, photoexposure, 40 partial curing, and the like. The thin layers constituting thick film insulative layer 18 contain a polymer of the formula indicated hereinabove. In one embodiment of the present invention, a first thin layer is applied to contact layer 16, said first thin layer containing a mixture of a polymer of the formula indicated hereinabove and an epoxy polymer, followed by photoexposure, partial curing, and subsequent application of one or more successive thin layers containing a polymer of the formula indicated hereinabove.

45 Figure 3 is a similar view to that of Figure 2 with a shallow anisotropically etched groove 40 in the heater plate, which is silicon, prior to formation of the underglaze 39 and patterning of the heating elements 34, electrodes 33 and common return 35. This recess 40 permits the use of only the thick film insulative layer 18 and eliminates the need for the usual electrode passivating layer 16. Since the thick film layer 18 is impervious to water and relatively thick (typically from about 20 to about 40 micrometers (microns), although the thickness can be outside this range), contamination 50 introduced into the circuitry will be much less than with only the relatively thin passivation layer 16 well known in the art. The heater plate is a fairly hostile environment for integrated circuits. Commercial ink generally entails a low attention to purity. As a result, the active part of the heater plate will be at elevated temperature adjacent to a contaminated aqueous ink solution which undoubtedly abounds with mobile ions. In addition, it is generally desirable to run the heater plate at a voltage of from about 30 to about 50 volts, so that there will be a substantial field present. Thus, the thick 55 film insulative layer 18 provides improved protection for the active devices and provides improved protection, resulting in longer operating lifetime for the heater plate.

When a plurality of lower substrates 28 are produced from a single silicon wafer, at a convenient point after the underglaze is deposited, at least two alignment markings (not shown) preferably are photolithographically produced

at predetermined locations on the lower substrates 28 which make up the silicon wafer. These alignment markings are used for alignment of the plurality of upper substrates 31 containing the ink channels. The surface of the single sided wafer containing the plurality of sets of heating elements is bonded to the surface of the wafer containing the plurality of ink channel containing upper substrates subsequent to alignment.

As disclosed in U.S. Patent 4,601,777 and U.S. Patent 4,638,337, the channel plate is formed from a two side polished, (100) silicon wafer to produce a plurality of upper substrates 31 for the printhead. After the wafer is chemically cleaned, a pyrolytic CVD silicon nitride layer (not shown) is deposited on both sides. Using conventional photolithography, a via for fill hole 25 for each of the plurality of channel plates 31 and at least two vias for alignment openings (not shown) at predetermined locations are printed on one wafer side. The silicon nitride is plasma etched off of the patterned vias representing the fill holes and alignment openings. A potassium hydroxide (KOH) anisotropic etch can be used to etch the fill holes and alignment openings. In this case, the [111] planes of the (100) wafer typically make an angle of about 54.7 degrees with the surface of the wafer. The fill holes are small square surface patterns, generally of about 20 mils (500 micrometers) per side, although the dimensions can be above or below this value, and the alignment openings are from about 60 to about 80 mils (1.5 to 3 millimeters) square, although the dimensions can be outside this range. Thus, the alignment openings are etched entirely through the 20 mil (0.5 millimeter) thick wafer, while the fill holes are etched to a terminating apex at about halfway through to three-quarters through the wafer. The relatively small square fill hole is invariant to further size increase with continued etching so that the etching of the alignment openings and fill holes are not significantly time constrained.

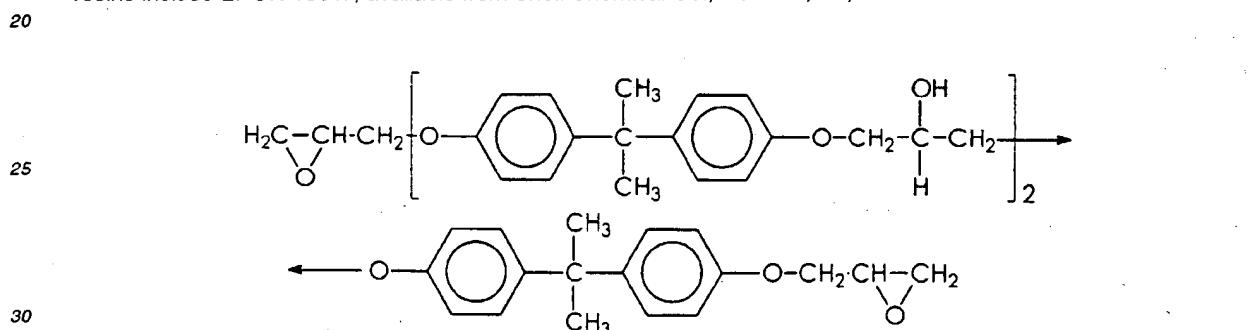
Next, the opposite side of the wafer is photolithographically patterned, using the previously etched alignment holes as a reference to form the relatively large rectangular recesses 24 and sets of elongated, parallel channel recesses that will eventually become the ink manifolds and channels of the printheads. The surface 22 of the wafer containing the manifold and channel recesses are portions of the original wafer surface (covered by a silicon nitride layer) on which an adhesive, such as a thermosetting epoxy, will be applied later for bonding it to the substrate containing the plurality of sets of heating elements. The adhesive is applied in a manner such that it does not run or spread into the grooves or other recesses. The alignment markings can be used with, for example, a vacuum chuck mask aligner to align the channel wafer on the heating element and addressing electrode wafer. The two wafers are accurately mated and can be tacked together by partial curing of the adhesive. Alternatively, the heating element and channel wafers can be given precisely diced edges and then manually or automatically aligned in a precision jig. Alignment can also be performed with an infrared aligner-bonder, with an infrared microscope using infrared opaque markings on each wafer to be aligned. The two wafers can then be cured in an oven or laminator to bond them together permanently. The channel wafer can then be milled to produce individual upper substrates. A final dicing cut, which produces end face 29, opens one end of the elongated groove 20 producing nozzles 27. The other ends of the channel groove 20 remain closed by end 21. However, the alignment and bonding of the channel plate to the heater plate places the ends 21 of channels 20 directly over elongated recess 38 in the thick film insulative layer 18 as shown in Figure 2 or directly above the recess 40 as shown in Figure 3 enabling the flow of ink into the channels from the manifold as depicted by arrows 23. The plurality of individual printheads produced by the final dicing are bonded to the daughter board and the printhead electrode terminals are wire bonded to the daughter board electrodes.

In one embodiment, a heater wafer with a phosphosilicate glass layer is spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in 95 parts methanol and 5 parts water, Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafer is then allowed to cool at 25°C for 5 minutes before spin coating the photoresist containing the photopatternable polymer onto the wafer at between 1,000 and 3,000 revolutions per minute for between 30 and 60 seconds. The photoresist solution is made by dissolving polyarylene ether ketone with 0.75 acryloyl groups and 0.75 chloromethyl groups per repeat unit and a weight average molecular weight of 25,000 in N-methylpyrrolidinone at 40 weight percent solids with Michler's ketone (1.2 parts ketone per every 10 parts of 40 weight percent solids polymer solution). The film is heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the film is covered with a mask and exposed to 365 nanometer ultraviolet light, amounting to between 150 and 1500 milliJoules per cm<sup>2</sup>. The exposed wafer is then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film is developed with 60:40 chloroform/cyclohexanone developer, washed with 90:10 hexanes/cyclohexanone, and then dried at 70°C for 2 minutes. A second developer/wash cycle is carried out if necessary to obtain a wafer with clean features. The processed wafer is transferred to an oven at 25°C, and the oven temperature is raised from 25 to 90°C at 2°C per minute. The temperature is maintained at 90°C for 2 hours, and then increased to 260°C at 2°C per minute. The oven temperature is maintained at 260°C for 2 hours and then the oven is turned off and the temperature is allowed to cool gradually to 25°C. When thermal cure of the photoresist films is carried out under an inert atmosphere, such as nitrogen or one of the noble gases, such as argon, neon, krypton, xenon, or the like, there is markedly reduced oxidation of the developed film and improved thermal and hydrolytic stability of the resultant devices. Moreover, adhesion of developed photoresist film is improved to the underlying substrate. If a second layer is spin coated over the first layer, the heat cure of the first developed layer can be stopped between 80 and 260°C before the second layer is spin coated onto the first layer.

A second thicker layer is deposited by repeating the above procedure a second time. This process is intended to be a guide in that procedures can be outside the specified conditions depending on film thickness and photoresist molecular weight. Films at 30 micrometers (microns) have been developed with clean features at 600 dots per inch.

For best results with respect to well-resolved features and high aspect ratios, photoresist compositions of the present invention are free of particulates prior to coating onto substrates. In one preferred embodiment, the photoresist composition containing the photopatternable polymer is subjected to filtration through a 2 micrometer (micron) nylon filter cloth (available from Tetko). The photoresist solution is filtered through the cloth under yellow light or in the dark as a solution containing from about 30 to about 60 percent by weight solids using compressed air (up to about 60 psi) and a pressure filtration funnel. No dilution of the photoresist solution is required, and concentrations of an inhibitor (such as, for example, MEHQ) can be as low as, for example, 500 parts per million or less by weight without affecting shelf life. No build in molecular weight of the photopatternable polymer is observed during this filtration process. While not being limited to any particular theory, it is believed that in some instances, such as those when unsaturated ester groups are present on the photopolymerizable polymer, compressed air yields results superior to those obtainable with inert atmosphere because oxygen in the compressed air acts as an effective inhibitor for the free radical polymerization of unsaturated ester groups such as acrylates and methacrylates.

In a particularly preferred embodiment, the photopatternable polymer is admixed with an epoxy resin in relative amounts of from about 75 parts by weight photopatternable polymer and about 25 parts by weight epoxy resin to about 90 parts by weight photopatternable polymer and about 10 parts by weight epoxy resin. Examples of suitable epoxy resins include EPON 1001F, available from Shell Chemical Co., Houston, TX, believed to be of the formula



as well as mixtures thereof. Curing agents such as the "Y" curative (meta-phenylenediamine) and the like, as well as mixtures thereof, can be used to cure the epoxy resin at typical relative amounts of about 10 weight percent curative per gram of epoxy resin solids. Process conditions for the epoxy resin blended with the photopatternable polymer are generally similar to those used to process the photoresist without epoxy resin. Preferably, the epoxy or epoxy blend is selected so that its curing conditions are different from the conditions employed to apply, image, develop, and cure the photopatternable polymer. Selective stepwise curing allows development of the photoresist film before curing the epoxy resin to prevent unwanted epoxy residues on the device. Incorporation of the epoxy resin into the photopatternable polymer material improves the adhesion of the photopatternable layer to the heater plate. Subsequent to imaging and during cure of the photopatternable polymer, the epoxy reacts with the heater layer to form strong chemical bonds with that layer, improving adhesive strength and solvent resistance of the interface. The presence of the epoxy may also improve the hydrophilicity of the photopatternable polymer and thus may improve the wetting properties of the layer, thereby improving the refill characteristics of the printhead.

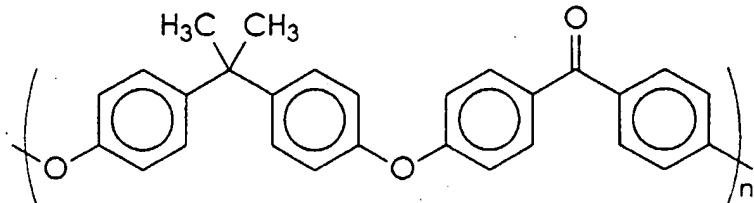
The printhead illustrated in Figures 1 through 3 constitutes a specific embodiment of the present invention. Any other suitable printhead configuration comprising ink-bearing channels terminating in nozzles on the printhead surface can also be employed with the materials disclosed herein to form a printhead of the present invention.

The present invention also encompasses printing processes with printheads according to the present invention. One embodiment of the present invention is directed to an ink jet printing process which comprises (1) providing an ink jet printhead comprising a plurality of channels, wherein the channels are capable of being filled with ink from an ink supply and wherein the channels terminate in nozzles on one surface of the printhead, said printhead comprising (i) an upper substrate with a set of parallel grooves for subsequent use as ink channels and a recess for subsequent use as a manifold, the grooves being open at one end for serving as droplet emitting nozzles, (ii) a lower substrate in which one surface thereof has an array of heating elements and addressing electrodes formed thereon, and (iii) a thick film layer deposited on the surface of the lower substrate and over the heating elements and addressing electrodes and patterned to form recesses therethrough to expose the heating elements and terminal ends of the addressing electrodes, said thick film layer comprising a crosslinked or chain extended photopatternable polymer of the formula indicated hereinabove, the upper and lower substrates being aligned, mated, and bonded together to form the printhead

with the grooves in the upper substrate being aligned with the heating elements in the lower substrate to form droplet emitting nozzles; (2) filling the channels with an ink; and (3) causing droplets of ink to be expelled from the nozzles onto a receiver sheet in an image pattern. A specific embodiment of this process is directed to a thermal ink jet printing process, wherein the droplets of ink are caused to be expelled from the nozzles by heating selected channels in an image pattern. The droplets can be expelled onto any suitable receiver sheet, such as fabric, plain paper such as Xerox® 4024 or 4010, coated papers, transparency materials, or the like.

**EXAMPLE I**

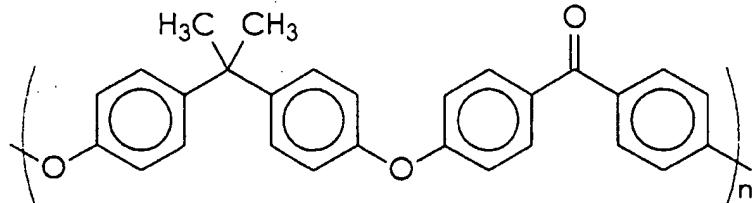
10 A polyarylene ether ketone of the formula



wherein n is between about 6 and about 30 (hereinafter referred to as poly(4-CPK-BPA)) was prepared as follows. A 1 liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 50 grams), bis-phenol A (Aldrich 23,965-8, 48.96 grams), potassium carbonate (65.56 grams), anhydrous N,N-dimethylacetamide (300 milliliters), and toluene (55 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours of heating at 175°C with continuous stirring, an aliquot of the reaction product that had been precipitated into methanol was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results:  $M_n$  4464,  $M_{peak}$  7583,  $M_w$  7927,  $M_z$  12,331, and  $M_{z+1}$  16,980. After 48 hours at 175°C with continuous stirring, the reaction mixture was filtered to remove potassium carbonate and precipitated into methanol. The polymer (poly(4-CPK-BPA)) was isolated in 86% yield after filtration and drying *in vacuo*. GPC analysis was as follows:  $M_n$  5347,  $M_{peak}$  16,126,  $M_w$  15,596,  $M_z$  29,209, and  $M_{z+1}$  42,710. The glass transition temperature of the polymer was about 120±10°C as determined using differential scanning calorimetry at a heating rate of 20°C per minute. Solution cast films from methylene chloride were clear, tough, and flexible. As a result of the stoichiometries used in the reaction, it is believed that this polymer had end groups derived from bis-phenol A.

**EXAMPLE II**

40 A polyarylene ether ketone of the formula



wherein n is between about 2 and about 30 (hereinafter referred to as poly(4-CPK-BPA)) was prepared as follows. A 5 liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 250 grams), bis-phenol A (Aldrich 23,965-8, 244.8 grams), potassium carbonate (327.8 grams), anhydrous N,N-dimethylacetamide (1,500 milliliters), and toluene (275 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 48 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered to remove insoluble salts, and the resultant solution was added to methanol to precipitate the polymer. The polymer was isolated by filtration, and the wet filter cake was

washed with water and then with methanol. The yield was 360 grams of vacuum dried product. The molecular weight of the polymer was determined by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results:  $M_n$  3,601,  $M_{peak}$  5,377,  $M_w$  4,311,  $M_z$  8,702, and  $M_{z+1}$  12,951. The glass transition temperature of the polymer was between 125 and 155°C as determined using differential scanning calorimetry at a heating rate of 5 20°C per minute dependent on molecular weight. Solution cast films from methylene chloride were clear, tough, and flexible. As a result of the stoichiometries used in the reaction, it is believed that this polymer had end groups derived from bis-phenol A.

### EXAMPLE III

10 A photoresist solution was prepared by dissolving a polyarylene ether ketone having 3 acrylate groups for every 4 repeating monomer units and 3 chloromethyl groups per repeating monomer unit and a weight average molecular weight of about 25,000 in N-methylpyrrolidone at 20 percent by weight solids. To 100 grams of this solution was added 15 a second solution containing 2 grams of EPON 1001 adhesive in 10 grams of N-methylpyrrolidone and a third solution containing 1 gram of "Y" curative (m-phenylenediamine) and 1 gram of Michler's ketone in 10 grams of N-methylpyrrolidone.

20 Phosphosilicate glass layers were spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in 95 parts methanol and 5 parts water, Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafers were then allowed to cool at 25°C for 5 minutes before spin coating onto 25 the wafers the photoresist solution prepared above at between 1,000 and 3,000 revolutions per minute for between 30 and 60 seconds. The films were heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the films were covered with masks and exposed to 365 nanometer ultraviolet light, amounting to between 150 and 1500 milliJoules per cm<sup>2</sup>. The exposed wafers were then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The films were developed with 60:40 chloroform/cyclohexanone developer, washed with 90:10 hexanes/cyclohexanone, and then dried at 70°C for 2 minutes. Half of the processed wafers were transferred to an oven at 25°C containing ordinary room air, and the other half of the processed wafers were transferred to an oven at 25°C containing an inert nitrogen atmosphere. The oven temperatures were raised from 25 to 120°C at a rate of 2°C per minute; thereafter the wafers in the oven were soaked in an ink comprising 30 7.5 percent by weight BASF Basacid Black X-34 dye, 10.5 percent by weight sulfolane, 15 percent by weight imidazole, 1 percent by weight imidazole hydrochloride, and 66 percent by weight water at 120°C for 2 hours, followed by heating the wafers in the oven from 120 to 260°C at a rate of 2°C per minute, soaking the wafers in ink for 2 hours at 260°C, and cooling the wafers to 25°C. Fourier Transform Infrared Spectroscopy indicated that the photoactive polyarylene ether ketone underwent substantial oxidation during the thermal curing under ordinary room air. The oxidation mechanism was substantially reduced or eliminated when the polyarylene ether ketone was cured under inert atmosphere. 35 In addition, the adhesion of the inert atmosphere-cured polyarylene ether ketone to the heater wafer was substantially superior to that of the air-cured polyarylene ether ketone to the heater wafer when soaked in ink at increased temperatures. Specifically, when soaked in an ink composition [comprising 10.0 percent by weight Projet Cyan 1 dye (10 percent by weight dye solids, obtained from Zeneca), 25.0 percent by weight Basacid Black NBX-34 dye (30 percent by weight dye solids, obtained from BASF), 21.0 percent by weight sulfolane (containing 95 percent by weight sulfolane, 40 5 percent by weight water, obtained from Phillips 66), 3.0 percent by weight trimethylolpropane (obtained from Aldrich Chemical Co.), 2.0 percent by weight polyacrylic acid (MW 2,000, obtained from Aldrich Chemical Co.), 1.0 percent by weight ammonium hydroxide (obtained from Fisher Scientific), 0.05 percent by weight polyethylene oxide (MW 18,500, obtained from Polysciences), and 37.95 percent by weight deionized water] at 60°C, the air cured films lifted from the heater wafer within 10 days at peel strengths of 1,000 psi or less, whereas the nitrogen cured films withstood 45 21 days in the ink without noticeable effect on the adhesion of the film to the heater wafer. Subsequent film coatings onto the inert atmosphere-cured layers also remained intact, indicating excellent adhesion to the nitrogen-cured polyarylene ether ketone layer.

### EXAMPLE IV

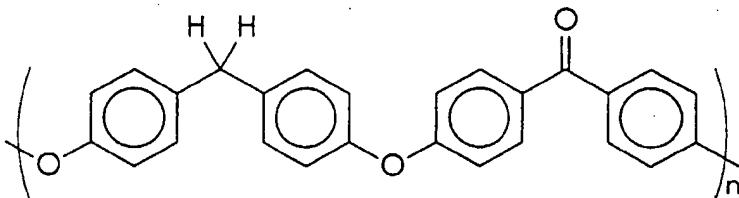
50 A solution was prepared containing a benzophenone-terminated, chloromethylated polyarylene ether ketone polymer having 0.5 chloromethyl groups per repeat unit in N-methylpyrrolidinone at a concentration of 33.7 percent by weight polymer solids. To this solution was added N,N-dimethyl ethyl methacrylate (obtained from Aldrich Chemical Co., Milwaukee, WI) in an amount of 6.21 percent by weight of the polymer solution, and the resulting solution was 55 stirred for 2 hours. The reaction of the chloromethyl groups with the N,N-dimethyl ethyl methacrylate occurred quickly, resulting in formation of a polymer having about 0.5 N,N-dimethyl ethyl methacrylate groups per monomer repeat unit.

The solution thus formed contained 40 percent by weight polymer solids. To this solution was added 1 part by weight Michler's ketone per 10 parts by weight of the 40 percent by weight solids solution. The resulting photoresist

solution was coated onto spinning silane-treated silicon wafers and the coated wafers were heated at 70°C for 10 minutes. The wafers were then allowed to cool to 25°C, followed by covering the wafers with masks and exposure to ultraviolet light at a wavelength of 365 nanometers, amounting to 200 milliJoules/cm<sup>2</sup>. The exposed films were then heated to 70°C for 5 minutes post exposure bake, followed by cooling to 25°C. The films were developed with 50:50 5 methanol/water developer and then dried at 70°C. The processed wafers were transferred to an oven at 25°C, and the oven temperature was raised at 2°C per minute to 90°C, maintained at 90°C for 2 hours, raised at 2°C per minute to 260°C, maintained at 260°C for 2 hours, and then allowed to cool to 25°C to effect post-cure. During post-cure, heat 10 stable, solvent resistant sites were formed. The post-cured, crosslinked polyarylene ether ketones were heat stable, chemically inert to thermal ink jet inks, electrically insulating, and mechanically robust, and exhibited low shrinkage during post-cure. Clean features were developed at resolutions of 300 and 600 dots per inch.

#### EXAMPLE V

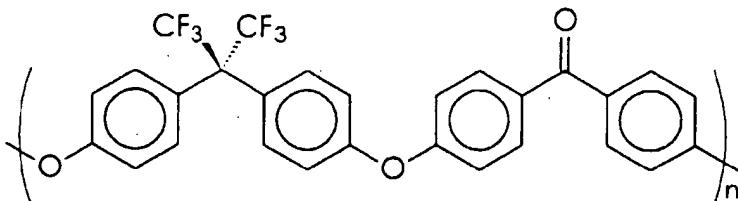
15 A polymer of the formula



25 wherein n represents the number of repeating monomer units was prepared as follows. A 500 milliliter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 16.32 grams, 0.065 mol), bis(4-hydroxyphenyl)methane (Aldrich, 14.02 grams, 0.07 mol), potassium carbonate (21.41 30 grams), anhydrous *N,N*-dimethylacetamide (100 milliliters), and toluene (100 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 48 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-CPK-BPM), was 24 grams. The polymer dissolved on heating in *N*-methylpyrrolidinone, *N,N*-dimethylacetamide, and 1,1,2,2-tetrachloroethane. The polymer remained soluble after the solution had cooled to 25°C.

#### EXAMPLE VI

35 A polymer of the formula



45 50 wherein n represents the number of repeating monomer units was prepared as follows. A 500 milliliter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 16.32 grams, 0.065 mol), hexafluorobisphenol A (Aldrich, 23.52 grams, 0.07 mol), potassium carbonate (21.41 grams), anhydrous *N,N*-dimethylacetamide (100 milliliters), and toluene (100 milliliters) were added to the flask and heated to 55 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 48 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-CPK-HFBPA), was 20 grams. The polymer was analyzed by gel permeation chromatography (gpc) (elution

solvent was tetrahydrofuran) with the following results:  $M_n$  1,975,  $M_{peak}$  2,281,  $M_w$  3,588, and  $M_{z+1}$  8,918.

**EXAMPLE VII**

5 The polymer poly(4-CPK-HFBPA), prepared as described in Example VI, was acryloylated with paraformaldehyde by the process described in Example II. Similar results were obtained.

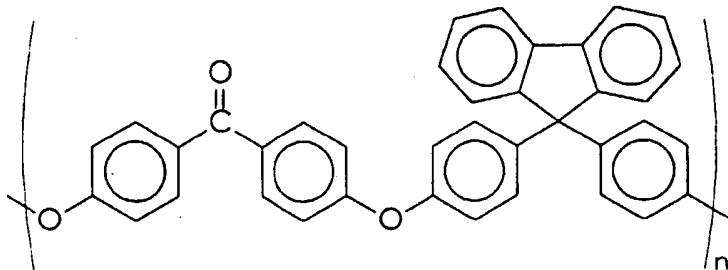
**EXAMPLE VIII**

10 The polymer poly(4-CPK-HFBPA), prepared as described in Example VI, is chloromethylated.

**EXAMPLE IX**

15 A polymer of the formula

20



25

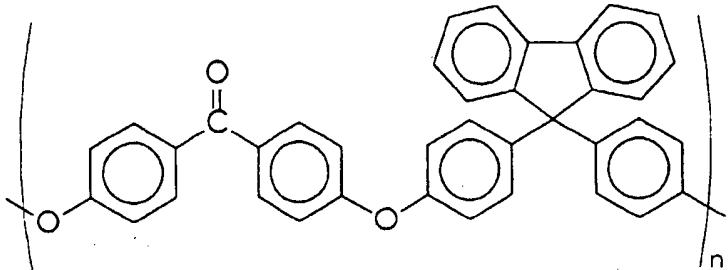
wherein n represents the number of repeating monomer units was prepared as follows. A 1-liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Difluorobenzophenone (Aldrich Chemical Co., Milwaukee, WI, 43.47 grams, 0.1992 mol), 9,9-bis(4-hydroxyphenyl)fluorenone (Ken Seika, Rumson, NJ, 75.06 grams, 0.2145 mol), potassium carbonate (65.56 grams), anhydrous *N,N*-dimethylacetamide (300 milliliters), and toluene (52 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 5 hours of heating at 175°C with continuous stirring, the reaction mixture was allowed to cool to 25°C. The solidified mass was treated with acetic acid (vinegar) and extracted with methylene chloride, filtered, and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-FPK-FBPA), was 71.7 grams. The polymer was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results:  $M_n$  59,100,  $M_{peak}$  144,000,  $M_w$  136,100,  $M_z$  211,350, and  $M_{z+1}$  286,100.

30

**EXAMPLE X**

40 A polymer of the formula

45



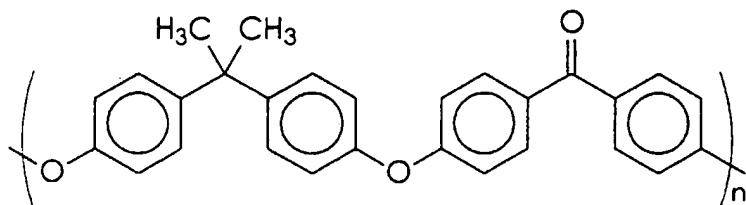
50

55 wherein n represents the number of repeating monomer units was prepared as follows. A 1-liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated

in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich Chemical Co., Milwaukee, WI, 50.02 grams, 0.1992 mol), 9,9-bis(4-hydroxyphenyl)fluorenone (Ken Seika, Rumson, NJ, 75.04 grams, 0.2145 mol), potassium carbonate (65.56 grams), anhydrous *N,N*-dimethylacetamide (300 milliliters), and toluene (52 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours 5 of heating at 175°C with continuous stirring, the reaction mixture was allowed to cool to 25°C. The reaction mixture was filtered and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-CPK-FBP), was 60 grams.

**EXAMPLE XI**

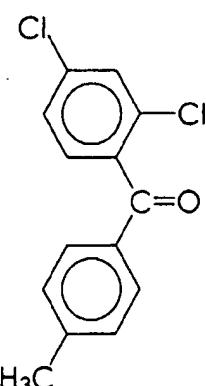
10 A polymer of the formula



wherein n represents the number of repeating monomer units was prepared as follows. A 1-liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated 25 in a silicone oil bath. 4,4'-Difluorobenzophenone (Aldrich Chemical Co., Milwaukee, WI, 16.59 grams), bisphenol A (Aldrich 14.18 grams, 0.065 mol), potassium carbonate (21.6 grams), anhydrous *N,N*-dimethylacetamide (100 milliliters), and toluene (30 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 4 hours of heating at 175°C with continuous stirring, the reaction mixture was allowed to cool to 25°C. The solidified mass was treated with acetic acid (vinegar) and extracted with 30 methylene chloride, filtered, and added to methanol to precipitate the polymer, which was collected by filtration, washed with water, and then washed with methanol. The yield of vacuum dried product, poly(4-FPK-BPA), was 12.22 grams. The polymer was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results:  $M_n$  5,158,  $M_{peak}$  15,080,  $M_w$  17,260, and  $M_{z+1}$  39,287. To obtain a lower molecular weight, the reaction can be repeated with a 15 mol% offset in stoichiometry.

35 **EXAMPLE XII**

40 4'-Methylbenzoyl-2,4-dichlorobenzene, of the formula

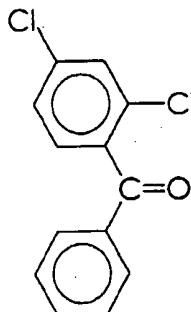


55 was prepared as follows. To a 2-liter flask equipped with a mechanical stirrer, argon inlet, Dean Stark trap, condenser, and stopper and situated in an oil bath was added toluene (152 grams). The oil bath temperature was raised to 130°C and 12.5 grams of toluene were removed. There was no indication of water. The flask was removed from the oil bath and allowed to cool to 25°C. 2,4-Dichlorobenzoyl chloride (0.683 mol, 143 grams) was added to form a solution. There-

after, anhydrous aluminum chloride (0.8175 mol, 109 grams) was added portion-wise over 15 minutes with vigorous gas evolution of hydrochloric acid as determined by odor. The solution turned orange-yellow and then red. The reaction was stirred for 16 hours under argon, and on removing the solvent, a solid lump was obtained. The mass was extracted with methylene chloride (1 liter), which was then dried over potassium carbonate and filtered. The filtrate was concentrated using a rotary evaporator and a vacuum pump to yield an oil which, upon cooling, became a solid crystalline mass. Recrystallization from methanol (1 liter) at -15°C gave 82.3 grams of 4'-methylbenzoyl-2,4-dichlorobenzene (melting point 55-56°C) in the first crop, 32 grams of product (from 500 milliliters of methanol) in the second crop, and 16.2 grams of product in the third crop. The total recovered product was 134.7 grams in 65.6% yield.

10 **EXAMPLE XIII**

Benzoyl-2,4-dichlorobenzene, of the formula



was prepared as follows. To a 2-liter flask equipped with a mechanical stirrer, argon inlet, Dean Stark trap, condenser, stopper and situated in an oil bath was added benzene (200 grams). The oil bath temperature was raised to 100°C and 19 grams of benzene were removed. There was no indication of water. The flask was removed from the oil bath and allowed to cool to 25°C. 2,4-Dichlorobenzoyl chloride (0.683 mol, 143 grams) was added to form a solution. Thereafter, anhydrous aluminum chloride (0.8175 mol, 109 grams) was added portion-wise over 15 minutes with vigorous gas evolution. Large volumes of hydrochloric acid were evolved as determined by odor. The solution turned orange-yellow and then red. The reaction was stirred for 16 hours under argon and was then added to 1 liter of ice water in a 2-liter beaker. The mixture was stirred until it became white and was then extracted with methylene chloride (1 liter). The methylene chloride layer was dried over sodium bicarbonate and filtered. The filtrate was concentrated using a rotary evaporator and a vacuum pump to yield an oil which, upon cooling, became a solid crystalline mass (154.8 grams). Recrystallization from methanol gave 133.8 grams of benzoyl-2,4-dichlorobenzene as white needles (melting point 41-43°C) in the first crop.

40 **EXAMPLE XIV**

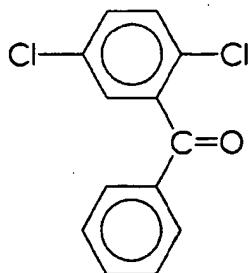
2,5-Dichlorobenzoyl chloride was prepared as follows. To a 2-liter, 3-neck round-bottom flask situated in an ice bath and equipped with an argon inlet, condenser, and mechanical stirrer was added 2,5-dichlorobenzoic acid (93.1 grams) in 400 milliliters of dichloromethane to form a slurry. Thionyl chloride (85 grams) in 68 grams of dichloromethane was then added and the mixture was stirred at 25°C. The mixture was then gradually heated and maintained at reflux for 16 hours. Thionyl chloride was subsequently removed using a Claisen distillation take-off head with heating to greater than 80°C. The reaction residue was transferred to a 500 milliliter 1-neck round bottom flask and then distilled using a Kugelrohr apparatus and a vacuum pump at between 70 and 100°C at 0.1 to 0.3 mm mercury to obtain 82.1 grams of 2,5-dichlorobenzoyl chloride, trapped with ice bath cooling as a yellow-white solid.

50 **EXAMPLE XV**

Benzoyl-2,5-dichlorobenzene, of the formula

5

10



was prepared as follows. To a 2-liter flask equipped with a mechanical stirrer, argon inlet, Dean Stark trap, condenser, and stopper and situated in an oil bath was added benzene (140 grams). The oil bath temperature was raised to 100°C and 19 grams of benzene were removed. There was no indication of water. The flask was removed from the oil bath and allowed to cool to 25°C. 2,5-Dichlorobenzoyl chloride (92.6 grams), prepared as described in Example XLII, was added to form a solution. Thereafter, anhydrous aluminum chloride (0.8175 mol, 109 grams) was cautiously added portion-wise over 15 minutes with vigorous gas evolution. Large volumes of hydrochloric acid were evolved as determined by odor. The solution turned orange-yellow and then red. The reaction was stirred for 16 hours under argon and was then added to 1 liter of ice water in a 2-liter beaker. The mixture was stirred until it became white and was then extracted with methylene chloride (1 liter). The methylene chloride layer was dried over sodium bicarbonate and filtered. The filtrate was concentrated using a rotary evaporator and a vacuum pump to yield crystals (103.2 grams). Recrystallization from methanol gave benzoyl-2,5-dichlorobenzene as white needles (melting point 85-87°C).

#### EXAMPLE XVI

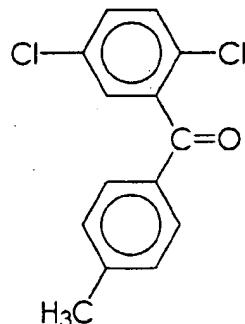
25

4'-Methylbenzoyl-2,5-dichlorobenzene, of the formula

30

35

40

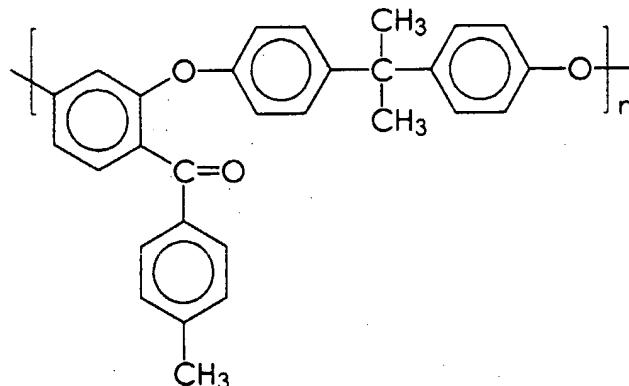


was prepared as follows. To a 2-liter flask equipped with a mechanical stirrer, argon inlet, Dean Stark trap, condenser, and stopper and situated in an oil bath was added toluene (200 grams). Thereafter, anhydrous aluminum chloride (64 grams) was cautiously added portion-wise over 15 minutes with vigorous gas evolution. Large volumes of hydrochloric acid were evolved as determined by odor. The solution turned orange-yellow and then red. The reaction was stirred for 16 hours under argon and was then added to 1 liter of ice water in a 2-liter beaker. The mixture was stirred until it became white and was then extracted with methylene chloride (1 liter). The methylene chloride layer was dried over sodium bicarbonate and filtered. The filtrate was concentrated using a rotary evaporator and a vacuum pump to yield crystals. Recrystallization from methanol gave 37.6 grams of 4'-methylbenzoyl-2,5-dichlorobenzene as light-yellow needles (melting point 107-108°C).

#### EXAMPLE XVII

55

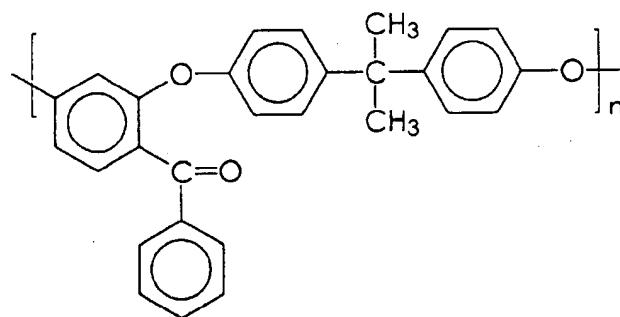
A polymer of the formula



wherein n represents the number of repeating monomer units was prepared as follows. A 250 milliliter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4'-Methylbenzoyl-2,4-dichlorobenzene (0.0325 mol, 8.6125 grams, prepared as described in Example XII), bis-phenol A (Aldrich 23,965-8, 0.035 mol, 7.99 grams), potassium carbonate (10.7 grams), anhydrous *N,N*-dimethylacetamide (60 milliliters), and toluene (60 milliliters, 49.1 grams) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours of heating at 175°C with continuous stirring, the reaction product was filtered and the filtrate was added to methanol to precipitate the polymer. The wet polymer cake was isolated by filtration, washed with water, then washed with methanol, and thereafter vacuum dried. The polymer (7.70 grams, 48% yield) was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results:  $M_n$  1,898,  $M_{peak}$  2,154,  $M_w$  2,470,  $M_z$  3,220, and  $M_{z+1}$  4,095.

#### EXAMPLE XVIII

30 A polymer of the formula



45 wherein n represents the number of repeating monomer units was prepared by repeating the process of Example XVII except that the 4'-methylbenzoyl-2,4-dichlorobenzene starting material was replaced with 8.16 grams (0.0325 mol) of benzoyl-2,4-dichlorobenzene, prepared as described in Example XIII, and the oil bath was heated to 170°C for 24 hours.

#### EXAMPLE XIX

50 A polymer having acryloylmethyl pendant groups thereon was prepared as follows. The polymer prepared as described in Example XVII (5 grams) in 1,1,2,2-tetrachloroethane (50 milliliters, 80.95 grams), paraformaldehyde (2.5 grams), p-toluenesulfonic acid monohydrate (0.5 gram), acrylic acid (7.9 grams) and crushed 4-methoxyphenol (MEHQ, 0.2 gram) were charged in a 6.5 fluid ounce beverage bottle equipped with a magnetic stirrer. The bottle was stoppered with a rubber septum and was then heated to 105°C in a silicone oil bath under argon using a needle inlet. The argon needle inlet was removed when the oil bath achieved 90°C. Heating at 105°C was continued with constant magnetic stirring for 1.5 hours. More MEHQ (0.2 gram) in 1 milliliter of tetrachloroethane was then added by syringe, and heating at 105°C with stirring was continued for 1.5 hours longer. The reaction mixture was initially a cloudy suspension which

became clear on heating. The reaction vessel was immersed as much as possible in the hot oil bath to prevent condensation of paraformaldehyde onto cooler surfaces of the reaction vessel. The reaction mixture was then allowed to return to 25°C and was filtered through a 25 to 50 micron sintered glass Buchner funnel. The reaction solution was added to methanol (1 gallon) to precipitate the polymer with acryloyl methyl group for every four repeat units.

The acryloylmethylated polymer was then dissolved in methylene chloride and reprecipitated into methanol (1 gallon) to yield 5 grams of fluffy white solid. The polymer was soluble in chlorinated solvents and polar aprotic solvents, but insoluble in acetone and alcohols. Films of the polymer were thermally ramp cured at 0.2°C per minute until 260°C was achieved, and then maintained at 260°C for 3 hours longer before the films were allowed to cool to 25°C.

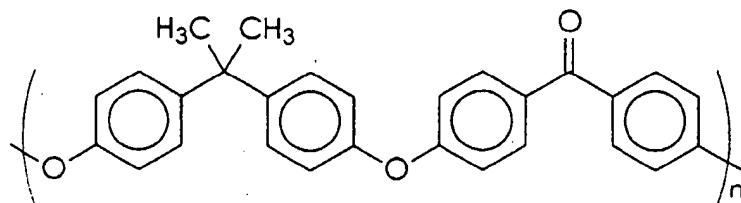
Photoactive compositions were made by preparing a 50 weight percent solids solution in N-methylpyrrolidinone using excess methylene chloride as a volatile diluent which was later removed. Michler's ketone was added to the formulation at between 0.5 and 1 weight percent of the resin solids. The solution was filtered and the methylene chloride was removed using a rotary evaporator. Solutions at approximately 37 weight percent solids were used to cast dried films of the polymer onto silicon wafers which had previously been treated with a silane adhesion promoter and heated at 70°C for 10 minutes. The wet films were dried at 80°C for 20 minutes before exposure to ultraviolet light. Ideal exposure conditions were about 2,500 milliJoules/cm<sup>2</sup>. After exposure, the films were heated to 80°C for 5 minutes before development with N-methylpyrrolidinone, cyclohexane, and methanol. Ten micron spin coated films were patterned at 300 dots per inch resolution.

#### EXAMPLE XX

The process of Example XIX was repeated except that the polymer prepared as described in Example XLVI was used. Similar results were obtained.

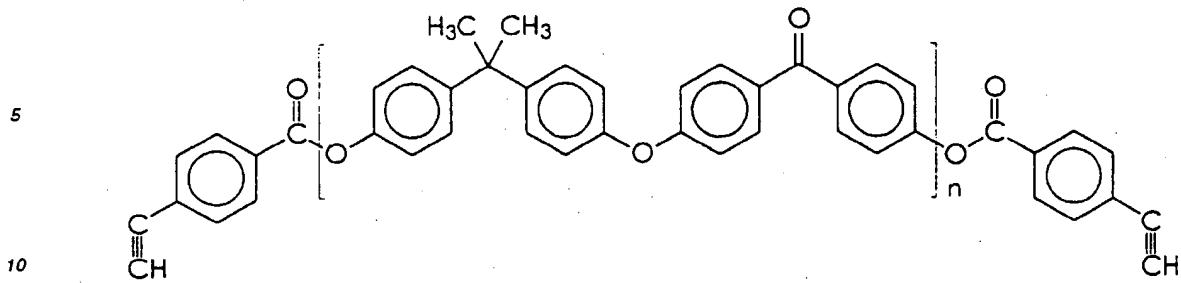
#### EXAMPLE XXI

A polymer of the formula



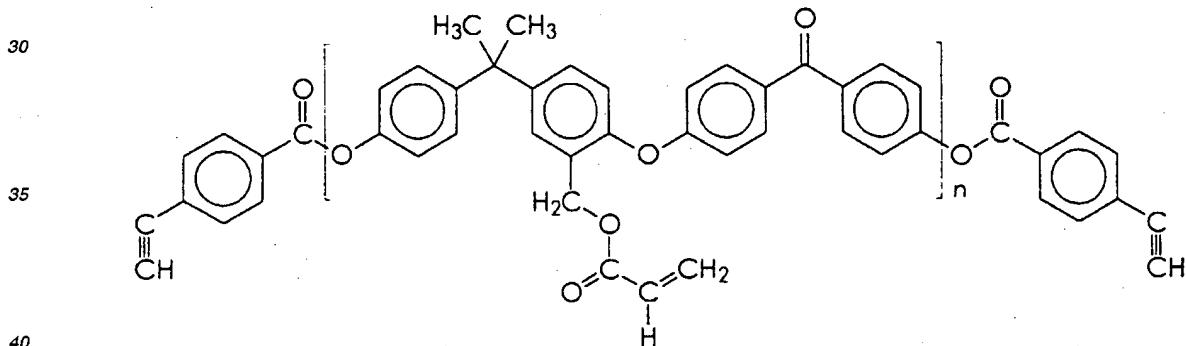
wherein n is about 9 (hereinafter referred to as poly(4-CPK-BPA)) was prepared as follows. A 500 milliliter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper was situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 16.32 grams, 0.065 mol), bis-phenol A (Aldrich 23,965-8, 15.98 grams, 0.07 mol), potassium carbonate (21.41 grams), anhydrous N,N-dimethylacetamide (100 milliliters), and toluene (100 milliliters) were added to the flask and heated to 175°C (oil bath temperature) while the volatile toluene component was collected and removed. After 24 hours of heating at 175°C with continuous stirring, the reaction mixture was filtered and added to methanol to precipitate a polymer which was collected by filtration, washed with water, and then washed with methanol. The vacuum dried product, poly(4-CPK-BPA), was 10.34 grams that was analyzed by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) with the following results: M<sub>n</sub> 4464, M<sub>peak</sub> 7580, M<sub>w</sub> 7930, M<sub>z</sub> 12,300, and M<sub>z+1</sub> 16,980. The glass transition temperature of the polymer was 155°C as determined using differential scanning calorimetry at a heating rate of 20°C per minute. Solution cast films from methylene chloride were clear, tough, and flexible. As a result of the stoichiometries used in the reaction, it is believed that this polymer had end groups derived from bis-phenol A.

To poly(4-CPK-BPA) (10 grams) thus prepared in chloroform (90 milliliters, extracted with water, dried over Drierite, filtered, and freshly distilled from Drierite) that contained a 50% molar excess of triethylamine (distilled over sodium hydride) was added 4-ethynylbenzoyl chloride (50 mol% excess) in chloroform (10 milliliters) with stirring under argon. After 3 hours, the polymer was added to methanol using a Waring blender to precipitate ethynyl-terminated poly(4-CPK-BPA), which was collected by filtration and was vacuum dried. The polymer was believed to be of the following formula:



wherein  $n$  is about 9.

15 Thereafter, ethynyl terminated poly(4-CPK-BPA) (10 grams) thus prepared in 1,1,2,2-tetrachloroethane (100 milliliters, 161.9 grams), paraformaldehyde (5 grams), p-toluenesulfonic acid monohydrate (1 gram), acrylic acid (15.8 grams), and crushed 4-methoxyphenol (MEHQ, 0.2 gram) were charged in a 6.5 fluid ounce beverage bottle equipped with a magnetic stirrer. The bottle was stoppered with a rubber septum and was then heated to 105°C in a silicone oil bath under argon using a needle inlet. The argon needle inlet was removed when the oil bath achieved 90°C. Heating at 105°C was continued with constant magnetic stirring for 1.5 hours. More MEHQ (0.2 gram) in 1 milliliter of 20 1,1,2,2-tetrachloroethane was then added by syringe, and heating at 105°C with stirring was continued for 1.5 hours longer. The reaction mixture was initially a cloudy suspension which became clear on heating. The reaction vessel was immersed as much as possible in the hot oil bath to prevent condensation of paraformaldehyde onto cooler surfaces of the reaction vessel. The reaction mixture was then allowed to return to 25°C and was filtered through a 25 to 50 25 micrometer (micron) sintered glass Buchner funnel. The reaction solution was added to methanol (1 gallon) to precipitate the polymer designated poly(acryloylmethyl-4-CPK-BPA), of the formula



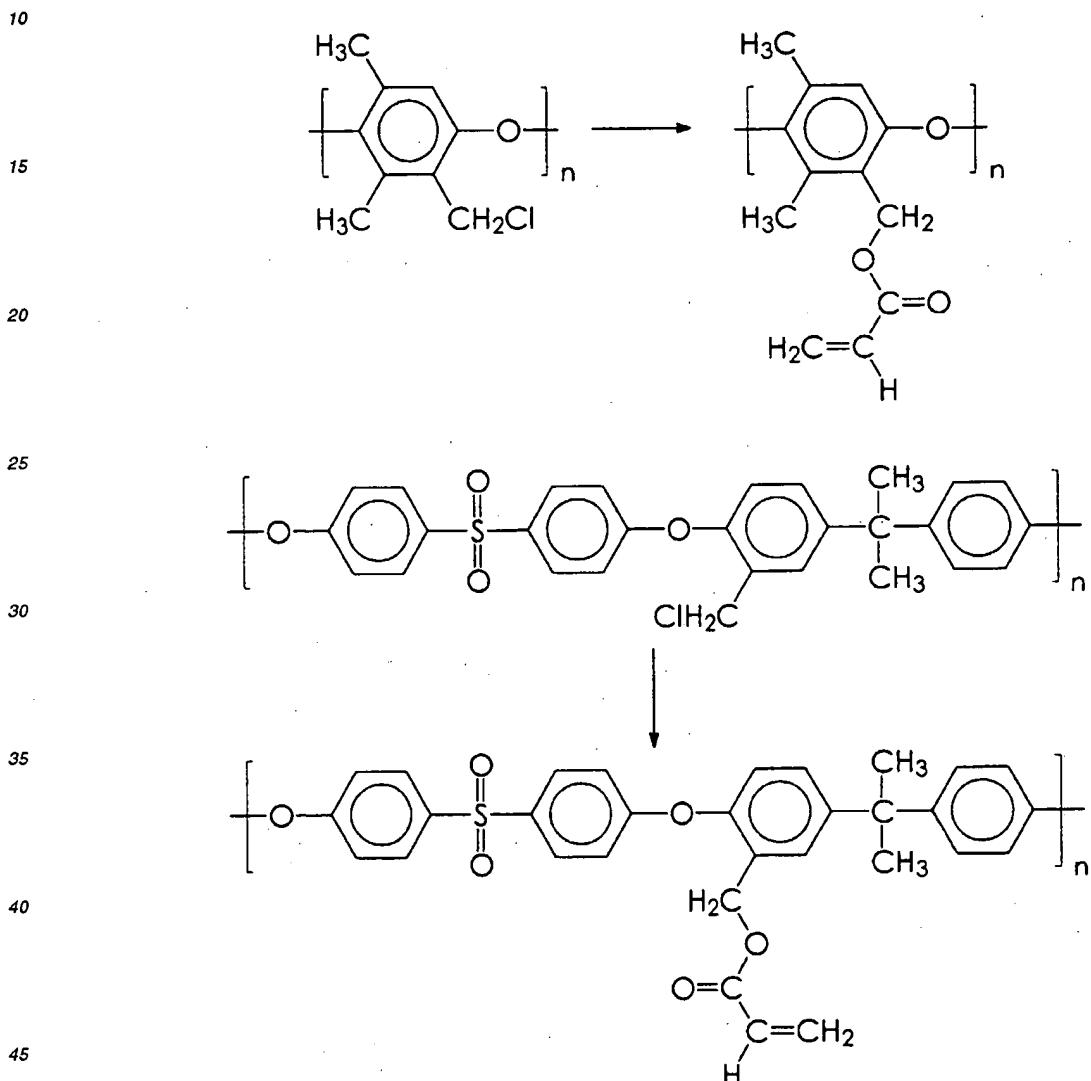
wherein n is about 9. <sup>1</sup>H NMR spectrometry was used to identify approximately 1 acryloylmethyl group for every four monomer (4-CPK-BPA) repeat units (i.e., a degree of acryloylation of 0.25). The poly(acryloylmethyl-4-CPK-BPA) was then dissolved in methylene chloride and reprecipitated into methanol (1 gallon) to yield 10 grams of fluffy white solid. The polymer was soluble in chlorinated solvents and polar aprotic solvents, but insoluble in acetone and alcohols. Films of the polymer were thermally ramp cured at 0.2°C per minute until 260°C was achieved, and then maintained at 260°C for 3 hours longer before the films were allowed to cool to 25°C.

Photoactive compositions were made by preparing a 50 weight percent solids solution in *N*-methylpyrrolidinone using excess methylene chloride as a volatile diluent which was later removed. Michler's ketone was added to the formulation at between 0.5 and 1 weight percent of the resin solids. The solution was filtered and the methylene chloride was removed using a rotary evaporator. Solutions at approximately 37 weight percent solids were used to cast dried films of the polymer onto silicon wafers which had previously been treated with a silane adhesion promoter and heated at 70°C for 10 minutes. The wet films were dried at 80°C for 20 minutes before exposure to ultraviolet light. Ideal exposure conditions were about 2,500 milliJoules/cm<sup>2</sup>. After exposure, the films were heated to 80°C for 5 minutes before development with *N*-methylpyrrolidinone, cyclohexane, and methanol. Thermal curing was then carried out by heating the films to 300°C. Ten micrometer (micron) spin coated films were patterned at 300 dots per inch resolution.

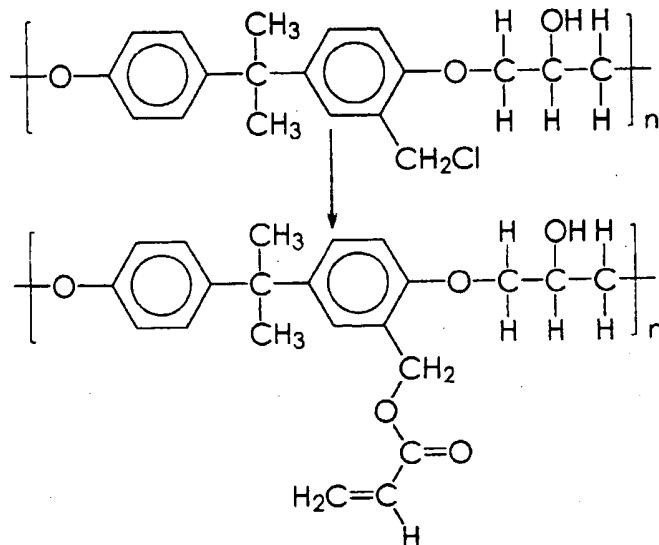
EXAMPLE XXII

Chloromethylated phenoxy resins, polyethersulfones, and polyphenylene oxides are prepared by reacting the un-substituted polymers with tin tetrachloride and 1-chloromethoxy-4-chlorobutane as described by W. H. Daly et al. in *Polymer Preprints*, 20(1), 835 (1979). The chloromethylation of polyethersulfone and polyphenylene oxide can also be accomplished as described by V. Percec et al. in *Makromol. Chem.*, 185, 2319 (1984).

5 Acryloylated polymers are then prepared as follows:



5



15

20

25

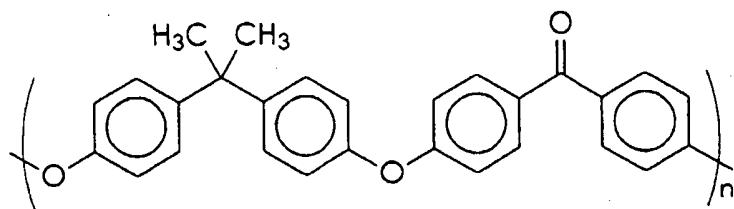
The chloromethylated polymers are acryloylated by allowing the chloromethylated polymer (10 grams) in N,N-dimethylacetamide (71 milliliters) to react with acrylic acid sodium salt (5.14 grams) for between 3 and 20 days, depending on the degree of acryloylation desired. Longer reaction times result in increased acrylate functionality.

#### EXAMPLE XXIII

A polymer of the formula

30

35



40

wherein n is about 9 (hereinafter referred to as poly(4-CPK-BPA)) having phenolic end groups is prepared as described in Example XLIX. In a flask equipped with a reflux condenser are placed 0.20 mol of phenol terminated poly(4-CPK-BPA), 0.23 mol of allyl bromide, 0.20 mole of potassium carbonate, and 200 milliliters of N,N-dimethylacetamide. The reaction mixture is heated at 60°C for 16 hours, cooled, and filtered. The filtrate is added to methanol to precipitate the polymer, poly(4-CPK-BPA) with allyl ether end groups.

45

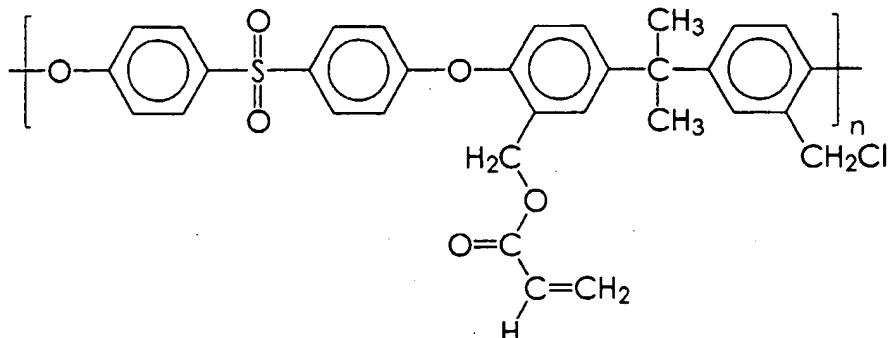
#### EXAMPLE XXIV

To allyl terminated polymer prepared as described in Example XIII (10 grams) in 200 grams of methylene chloride is added drop-wise *m*-chloroperoxybenzoic acid (2 equivalents) in 25 grams of methylene chloride over 15 minutes. The reaction solution is magnetically stirred for 16 hours, and then is added to 5% aqueous sodium bicarbonate. The methylene chloride layer is removed using a rotary evaporator, and the polymer that coagulates is dissolved in methylene chloride, precipitated into methanol, filtered and vacuum dried to yield 8 grams of epoxy terminated poly(4-CPK-BPA).

#### EXAMPLE XXV

A hydroxy-terminated polyether sulfone is made with a number average molecular weight of 2,800 following the

procedure described in V. Percec and B. C. Auman, *Makromol. Chem.*, **185**, 617 (1984). This polymer is chloromethylated as described in V. Percec and B. C. Auman, *Makromol. Chem.*, **185**, 2319 (1984). The polyether sulfone with 1.5 chloromethyl groups per repeat unit (10 grams) in 71 milliliters of *N,N*-dimethylacetamide is magnetically stirred with sodium acrylate (5.74 grams) for 112 hours at 25°C. The mixture is centrifuged, and the supernate is added to 5 methanol using a Waring blender to precipitate the polymer, which is filtered and vacuum dried. About 50% of the chloromethyl groups are replaced with acryloyl groups. The product has the following formula:



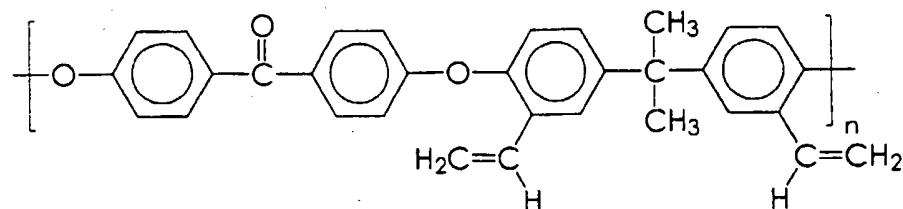
This polymer when formulated at 40 weight percent solids with Michler's ketone at about 0.5 weight percent with 3 weight percent benzophenone is a suitable photoresist for preparing thermal ink jet heads. A heater wafer with a phosphosilicate glass layer is spin coated with a solution of Z6020 adhesion promoter (0.01 weight percent in methanol 25 (95 parts) and water (5 parts), available from Dow Corning) at 3000 revolutions per minute for 10 seconds and dried at 100°C for between 2 and 10 minutes. The wafer is then allowed to cool at 25°C over 5 minutes before spin coating the polymer photoresist onto the wafer at between 1000 and 3000 revolutions per minute for between 30 and 60 30 seconds. The photoresist solution is made by dissolving polyarylene ether sulfone with 0.75 acryloyl groups and 0.75 chloromethyl groups per repeat unit and a weight average molecular weight of 25,000 in *N*-methylpyrrolidinone at 40 weight percent solids with Michler's ketone (1.2 parts per every 10 parts of 40 weight percent solids solution). The film 35 is heated (soft baked) in an oven for between 10 and 15 minutes at 70°C. After cooling to 25°C over 5 minutes, the film is covered with a mask and exposed to 365 nanometers ultraviolet light, amounting to between 150 and 1500 millijoules per cm<sup>2</sup>. The exposed wafer is then heated at 70°C for 2 minutes post exposure bake, followed by cooling to 25°C over 5 minutes. The film is developed with 6:4 chloroform/cyclohexanone developer, washed with 9:1 hexanes/ 40 cyclohexanone and then dried at 70°C for 2 minutes. A second developer/wash cycle is carried out if necessary to obtain a wafer with clean features. The processed wafer is transferred to an oven at 25°C, and the oven temperature is raised from 25 to 90°C at 2°C per minute. The temperature is maintained at 90°C for 2 hours, and then increased to 260°C at 2°C per minute. The oven temperature is maintained at 260°C for 2 hours, and the oven is then turned off and the temperature is allowed to cool gradually to 25°C. When thermal cure of the photoresist films is carried out 45 under inert atmosphere such as argon or nitrogen, there is markedly reduced oxidation of the developed film and improved thermal and hydrolytic stability of the resultant devices. Moreover, adhesion is improved to the underlying substrate. The heat cure of the first developed layer can be stopped between 80 and 260°C before the second layer is spin coated on top. A second thicker layer is deposited by repeating the above procedure a second time. This process is intended to be a guide in that procedures can be outside the specified conditions depending on film thickness and photoresist molecular weight. Films at 30 micrometers (microns) are developable with clean features at 300 dots per inch.

#### EXAMPLE XXVI

50 Poly(4-CPK-BPA) is made with a number average molecular weight of 2,800 as follows. A 5-liter, 3-neck round-bottom flask equipped with a Dean-Stark (Barrett) trap, condenser, mechanical stirrer, argon inlet, and stopper is situated in a silicone oil bath. 4,4'-Dichlorobenzophenone (Aldrich 11,370, Aldrich Chemical Co., Milwaukee, WI, 250 grams), bis-phenol A (Aldrich 23,965-8, 244.8 grams), potassium carbonate (327.8 grams), anhydrous *N,N*-dimethylacetamide (1,500 milliliters), and toluene (275 milliliters) are added to the flask and heated to 175°C (oil bath temperature 55) while the volatile toluene component is collected and removed. After hours of heating 30 hours at 175°C with continuous stirring, the reaction mixture is filtered to remove insoluble salts, and the resultant solution is added to methanol (5 gallons) to precipitate the polymer. The polymer is isolated by filtration, and the wet filter cake is washed with water (3 gallons) and then with methanol (3 gallons). The yield is about 360 grams of vacuum dried polymer. It is

believed that if the molecular weight of the polymer is determined by gel permeation chromatography (gpc) (elution solvent was tetrahydrofuran) the following results will be obtained:  $M_n$  2,800,  $M_{peak}$  5,800,  $M_w$  6,500,  $M_z$  12,000 and  $M_{z+1}$  17,700. As a result of the stoichiometries used in the reaction, it is believed that this polymer has end groups derived from bis-phenol A.

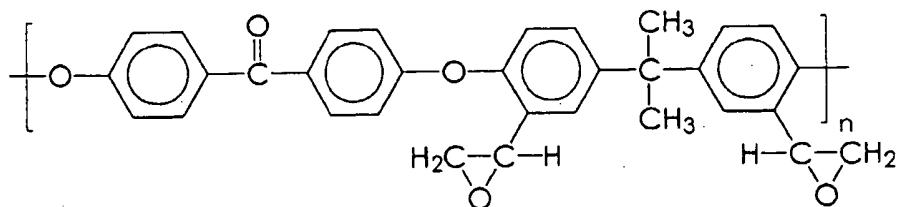
5 The polymer is then chloromethylated as follows. A solution of chloromethyl ether in methyl acetate is made by adding 282.68 grams (256 milliliters) of acetyl chloride to a mixture of dimethoxy methane (313.6 grams, 366.8 milliliters) and methanol (10 milliliters) in a 5-liter 3-neck round-bottom flask equipped with a mechanical stirrer, argon inlet, reflux condenser, and addition funnel. The solution is diluted with 1,066.8 milliliters of 1,1,2,2-tetrachloroethane and then tin tetrachloride (2.4 milliliters) is added via a gas-tight syringe, along with 1,1,2,2-tetrachloroethane (133.2 milliliters) using an addition funnel. The reaction solution is heated to 50°C and a solution of poly(4-CPK-BPA) (160.8 grams) in 1,1,2,2-tetrachloroethane (1,000 milliliters) is rapidly added. The reaction mixture is then heated to reflux with an oil bath set at 110°C. After four hours reflux with continuous stirring, heating is discontinued and the mixture is allowed to cool to 25°C. The reaction mixture is transferred in stages to a 2 liter round bottom flask and concentrated using a rotary evaporator with gentle heating up to 50°C and reduced pressure maintained with a vacuum pump trapped with liquid nitrogen. The concentrate is added to methanol (6 gallons) to precipitate the polymer using a Waring blender. The polymer is isolated by filtration and vacuum dried to yield 200 grams of poly(4-CPK-BPA) with 1.5 chloromethyl groups per repeat unit. Solvent free polymer is obtained by reprecipitation of the polymer (75 grams) dissolved in methylene chloride (500 grams) into methanol (3 gallons) followed by filtration and vacuum drying to yield 70.5 grams (99.6% yield) of solvent free polymer. To a solution of the chloromethylated poly(4-CPK-BPA) (192 mmol of chloromethyl groups) in 80 milliliters of dioxane is added 12 grams (46 mmol) of triphenylphosphine. After 15 hours of reflux with mechanical stirring and cooling to 25°C, the polymer solidifies and the mixture is extracted with diethyl ether using a Waring blender. The yellow product is filtered, washed several times with diethyl ether, and vacuum dried. To a solution of triphenylphosphonium chloride salt of chloromethylated poly(4-CPK-BPA) (14 mmol of phosphonium groups) in 200 milliliters of methanol, 2 milliliters of Triton B (40 weight percent aqueous solution) and 11.5 milliliters (140 mmol) of 26 formaldehyde (37 weight percent aqueous solution) are added. The stirred reaction mixture is treated slowly with 36 milliliters of 50 weight percent aqueous sodium hydroxide. A precipitate starts to appear on addition of the first drops of sodium hydroxide solution. After 10 hours of reaction at 25°C, the precipitate is filtered and vacuum dried. The separated polymer is dissolved in methylene chloride, washed several times with water, and then precipitated with methanol. Alternatively, to a solution of solution of 1.8 mmol of phosphonium groups of the triphenylphosphonium chloride salt chloromethylated poly(4-CPK-BPA) in 40 milliliters of methylene chloride at ice-water temperature, 1.6 milliliters (19.5 mmol) of formaldehyde (37 weight percent aqueous solution), and 0.4 milliliters of Triton-B (40 weight percent aqueous solution) is added. The stirred reaction mixture is treated slowly with 5 milliliters (62.5 mmol) of 50 weight percent aqueous sodium hydroxide. After all the hydroxide solution is added, the reaction mixture is allowed to react at 25°C. After 7 hours of reaction, the organic layer is separated, washed with dilute hydrochloric acid, then washed with water, and then precipitated into methanol from chloroform. The polymer has the structure:



45

The polymer can be further treated with m-chloroperoxybenzoic acid to form an epoxidized product with the following formula:

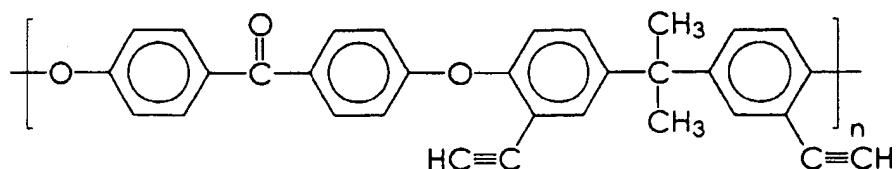
50



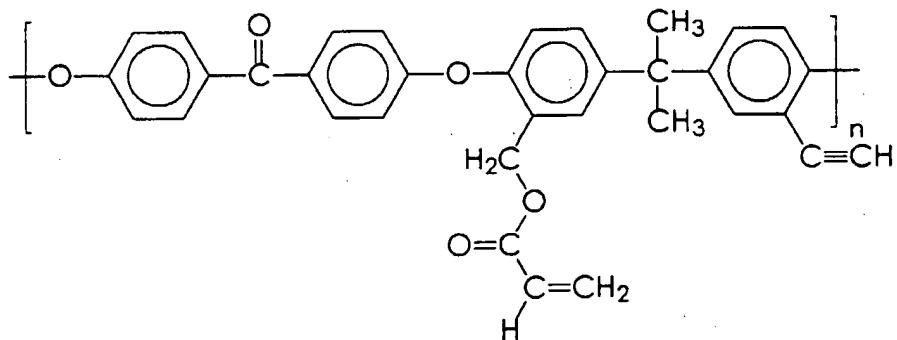
55

**EXAMPLE XXVII**

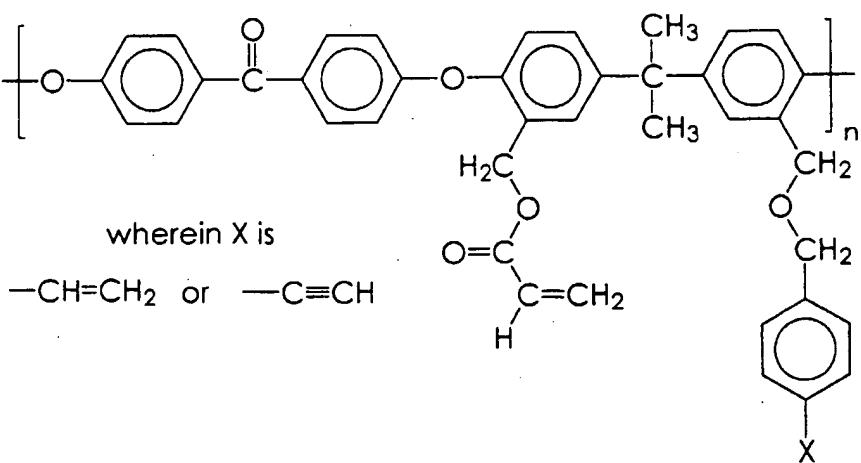
5 A solution of poly(4-CPK-BPA) with pendant vinyl groups (prepared as described in Example LIV, 12.5 mmol of vinyl groups) in 30 milliliters of methylene chloride is cooled in an ice-water bath and titrated with bromine until an orange color persists, indicating addition of bromine across the double bond and conversion of the ethylene groups to 1,2-bromoethyl groups. After 30 minutes of stirring at 25°C, the polymer is precipitated with methanol, filtered, and vacuum dried. To a vigorously stirred mixture of 3 mmol of 1,2-bromoethyl groups of 1,2-dibromoethylated poly(4-CPK-BPA) in 30 milliliters of methylene chloride and 10 milliliters of 50 weight percent aqueous sodium hydroxide at 25°C, 3 grams (9 mmol) of tetrabutylammonium hydroxide are added. An exothermic reaction takes place, indicating generation of NaBr and H<sub>2</sub>O and conversion of the 1,2-bromoethyl groups to ethynyl groups. After 1.5 hours of stirring at 25°C, the organic portion is washed with water, dilute hydrochloric acid, then water, and then methanol. The white poly (4-CPK-BPA) is precipitated from methylene chloride into methanol. Alternatively, to a stirred solution at 25°C, 3 mmol of 1,2-dibromoethyl groups of bromoethylated poly(4-CPK-BPA) in 20 milliliters of DMSO, 1.4 grams (12 mmol) of potassium t-butoxide in 5 milliliters of dimethyl sulfoxide is added. The reaction mixture is stirred at 25°C for 1 hour and then precipitated into methanol, filtered, and vacuum dried. The soluble part of this polymer is extracted with methylene chloride or chloroform and precipitated into methanol. The product has the formula



25 Polymers with the following formulae can also be made by the procedures described hereinabove:



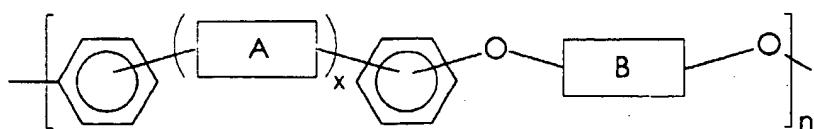
wherein X is



In each instance, the polymer is first substituted with the ethynyl or vinyl groups and then substituted with the unsaturated ester groups. The polymer can be substituted with vinyl groups by reacting the haloalkylated polymer with triphenyl phosphine to generate the triphenylphosphonium-substituted polymer, followed by reaction of the triphenylphosphonium-substituted polymer with formaldehyde in the presence of a base to generate the vinyl-substituted polymer. Ethynyl and vinyl terminated poly(4-CPK-BPA) can be made by substituting poly(4-CPK-BPA) for hydroxy terminated pol-  
5 ether sulfone in the procedures described by V. Percec and B. C. Auman, *Makromol. Chem.*, **185**, 1867 (1984).

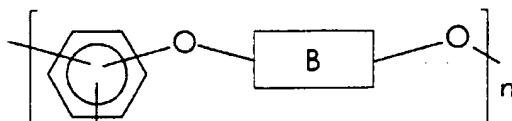
## Claims

10 1. A composition comprising a polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation, said polymer being of the formula

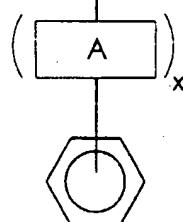


20

or

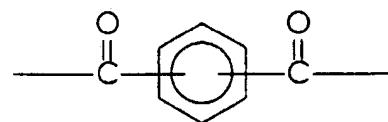


30

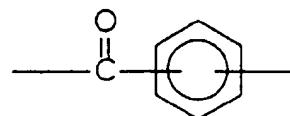


35

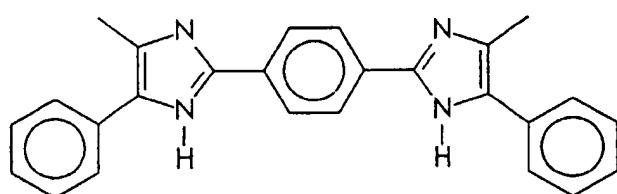
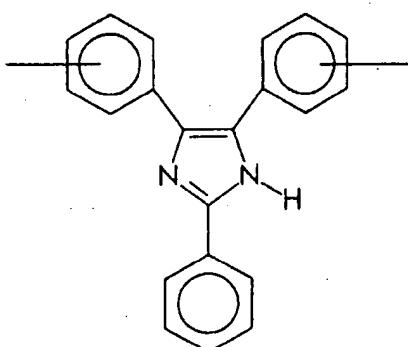
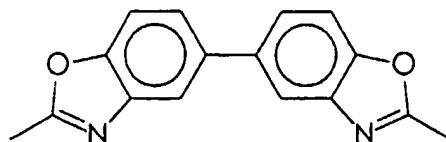
wherein x is an integer of 0 or 1, A is



45



55



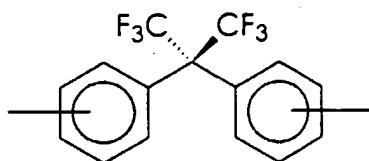
40

-O-,

-C(CH<sub>3</sub>)<sub>2</sub>-

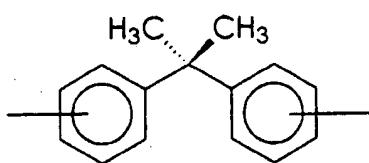
45

or mixtures thereof, B is



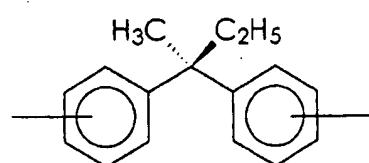
55

5



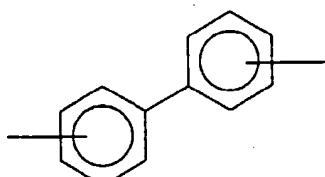
10

15

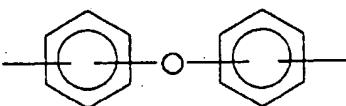


20

25

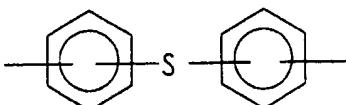


30

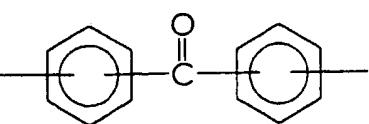


35

40

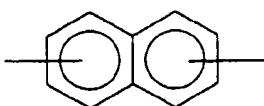


45

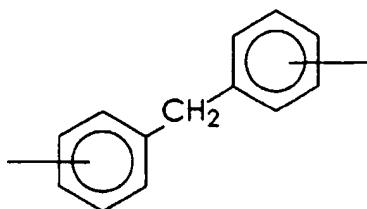


50

55

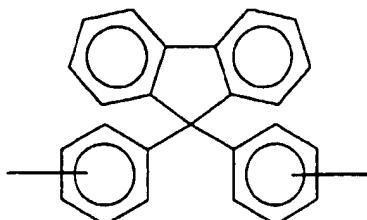


5



10

15



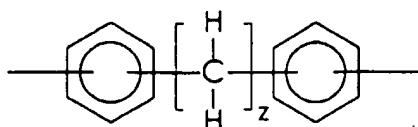
20



25

wherein  $v$  is an integer of from 1 to about 20,

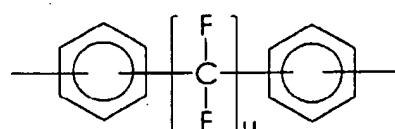
30



35

wherein  $z$  is an integer of from 2 to about 20,

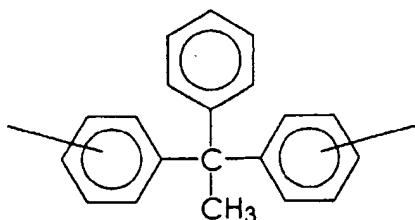
40



45

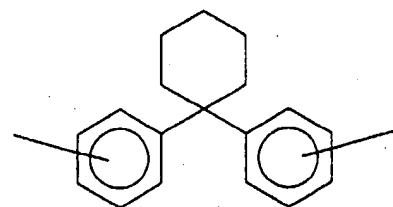
wherein  $u$  is an integer of from 1 to about 20,

50



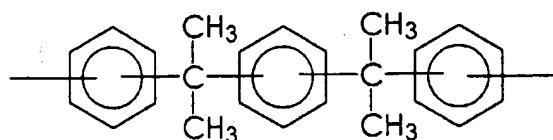
55

5



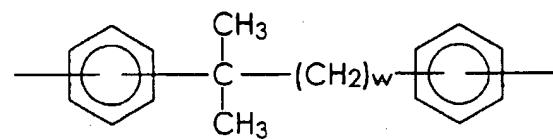
10

15



20

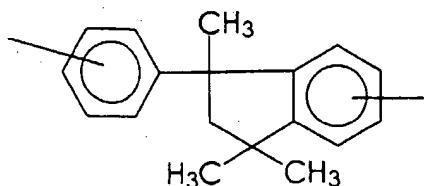
25



wherein w is an integer of from 1 to about 20,

30

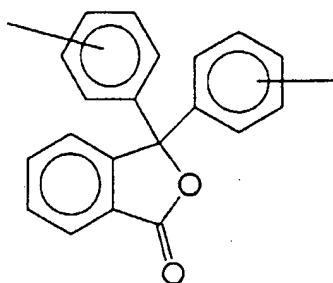
35



40

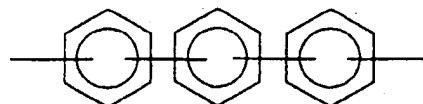
45

50

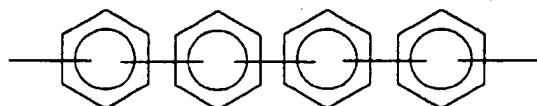


55

5



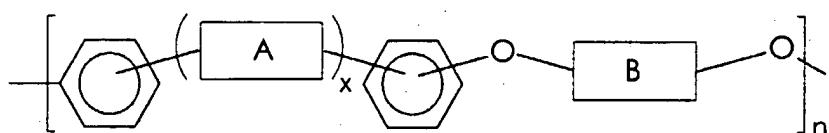
10



15 or mixtures thereof, and n is an integer representing the number of repeating monomer units.

2. A composition which comprises a crosslinked or chain extended polymer of the formula

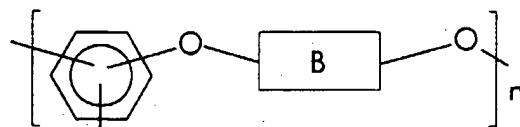
20



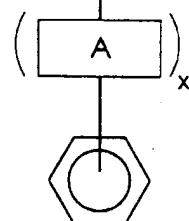
25

or

30



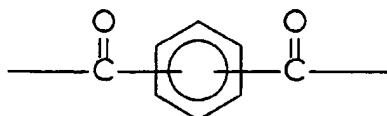
35



40

wherein x is an integer of 0 or 1, A is

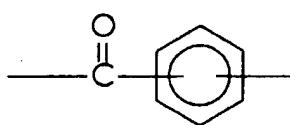
45



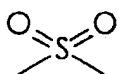
50

55

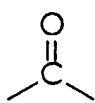
5



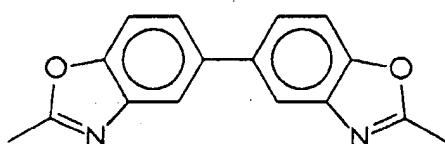
10



15

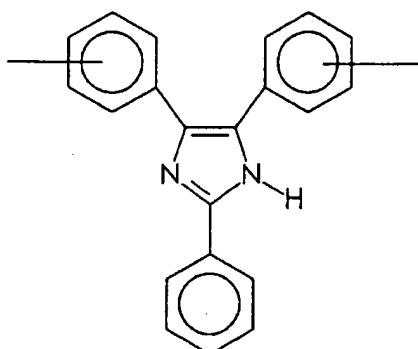


20



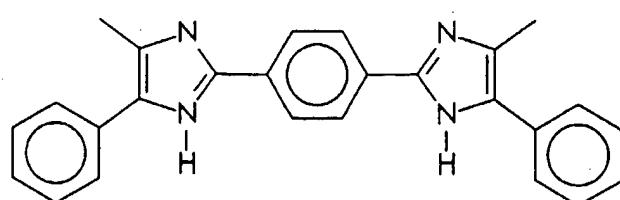
25

30



35

40



50

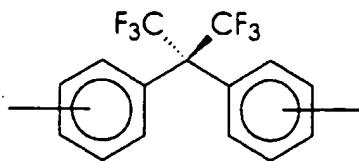
-O-,

55

-C(CH<sub>3</sub>)<sub>2</sub>-,

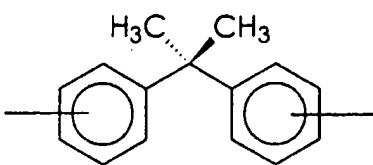
or mixtures thereof, B is

5



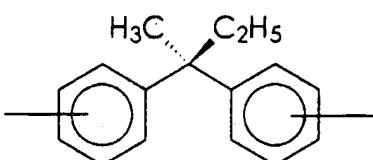
10

15



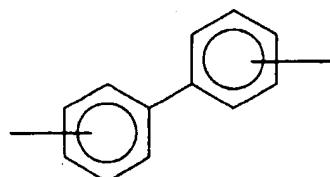
20

25



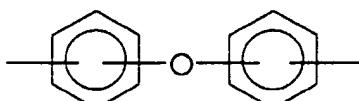
30

35



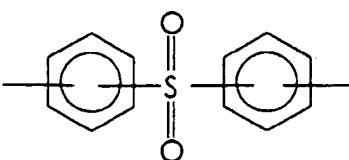
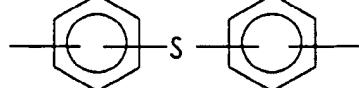
40

45

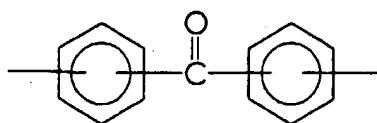


50

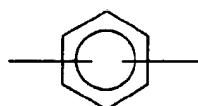
55



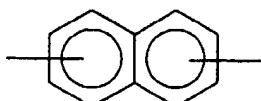
5



10

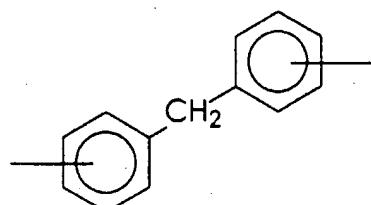


15



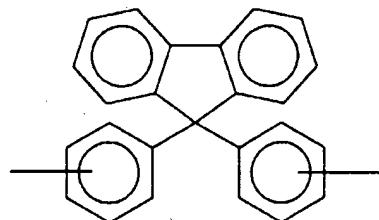
20

25



30

35



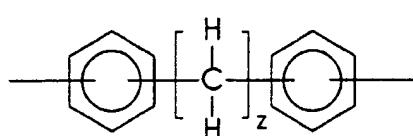
40

45



wherein  $v$  is an integer of from 1 to about 20,

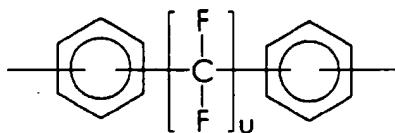
50



55

wherein  $z$  is an integer of from 2 to about 20,

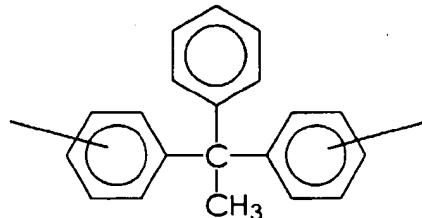
5



wherein u is an integer of from 1 to about 20,

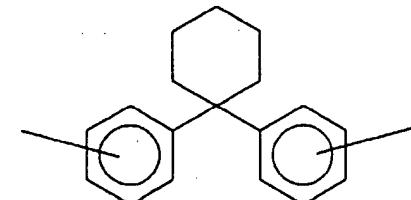
10

15



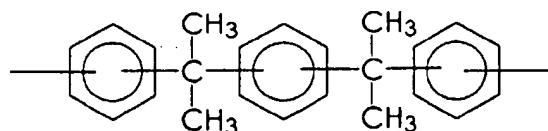
20

25



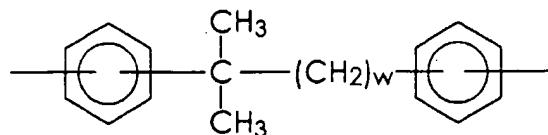
30

35



40

45

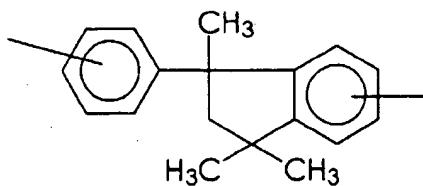


wherein w is an integer of from 1 to about 20,

50

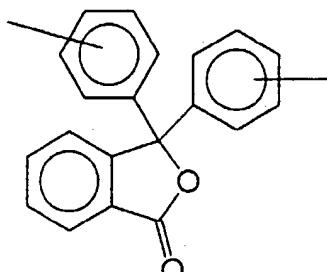
55

5



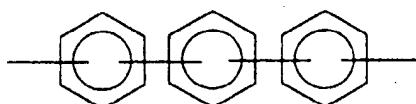
10

15



20

25



30

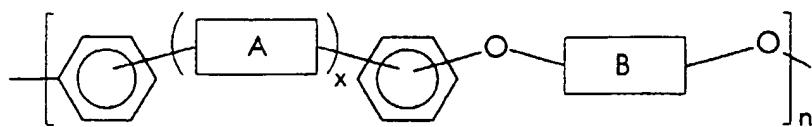
35



or mixtures thereof, and n is an integer representing the number of repeating monomer units, said crosslinking or chain extension occurring through photosensitivity-imparting substituents contained on at least some of the monomer repeat units of the polymer which form crosslinks or chain extensions in the polymer upon exposure to actinic radiation.

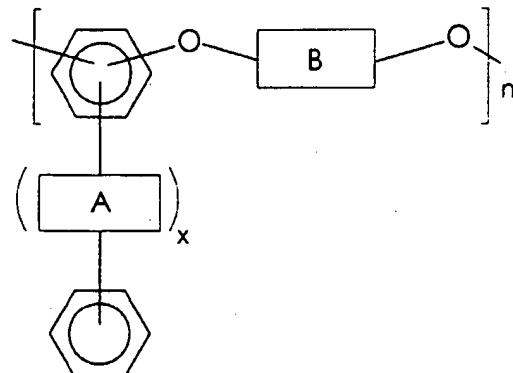
- 40 3. A composition according to claim 2 wherein the crosslinks or chain extensions in the crosslinked or chain extended polymer are via methylene groups.
- 45 4. A composition according to any of claims 1 to 3 wherein the polymer has end groups derived from the "A" groups of the polymer.
- 50 5. A composition according to any of claims 1 to 3 wherein the polymer has end groups derived from the "B" groups of the polymer.
6. A composition according to any of claims 1 to 5, wherein A is selected so that the repeat unit contains a benzophenone moiety.
- 55 7. A process which comprises the steps of (a) providing a polymer containing at least some monomer repeat units with photosensitivity-imparting substituents which enable crosslinking or chain extension of the polymer upon exposure to actinic radiation, said polymer being of the formula

5



or

10



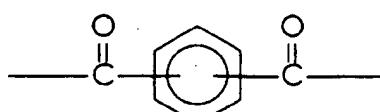
15

20

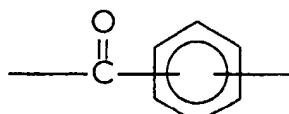
wherein x is an integer of 0 or 1, A is

25

30

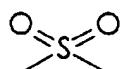


35



40

45

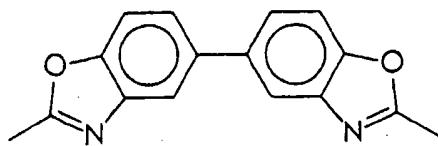


50

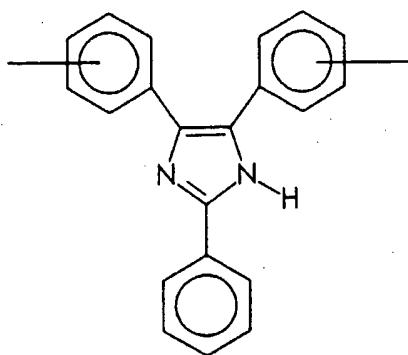


55

5

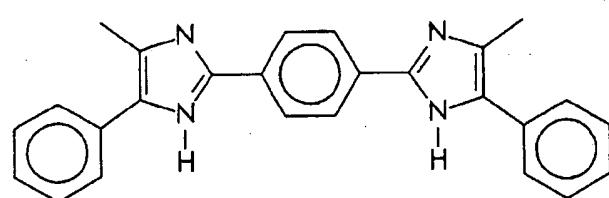


10



15

20



25

30

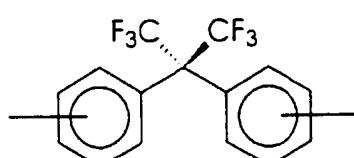
-O-,

-C(CH<sub>3</sub>)<sub>2</sub>-

40

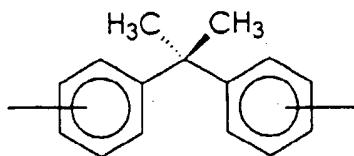
or mixtures thereof, B is

45

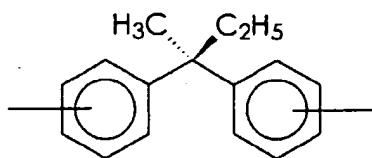


50

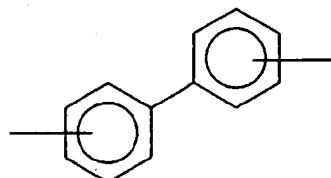
55



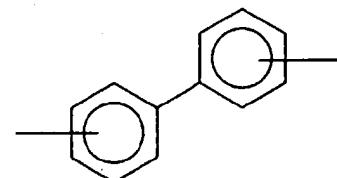
5



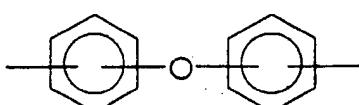
10



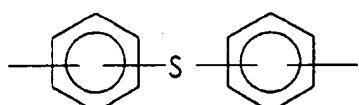
15



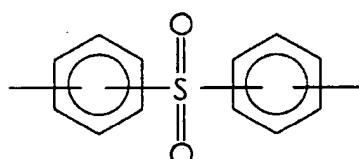
20



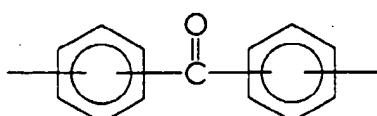
25



30

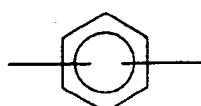


35



40

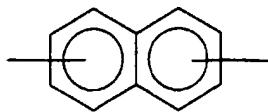
45



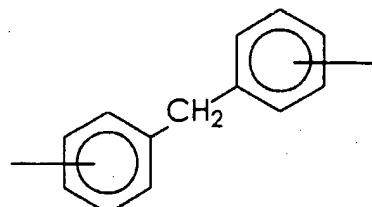
50

55

5

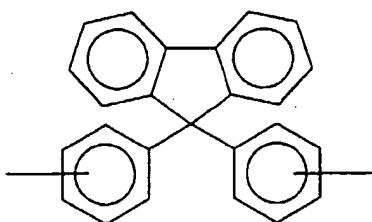


10



15

20



25

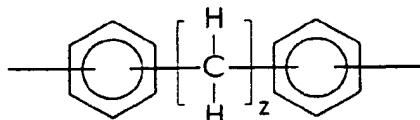
30



35

wherein v is an integer of from 1 to about 20,

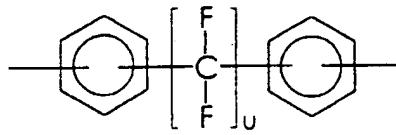
40



45

wherein z is an integer of from 2 to about 20,

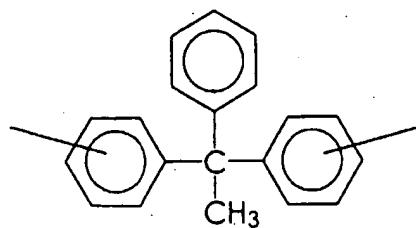
50



55

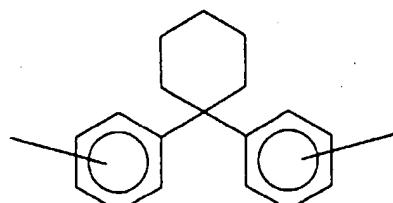
wherein u is an integer of from 1 to about 20,

5



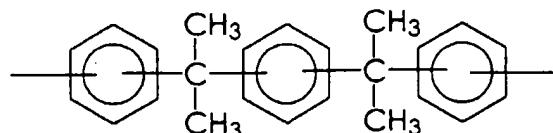
10

15



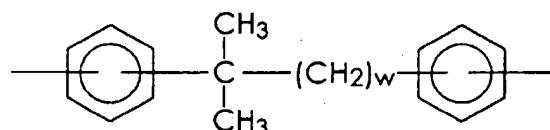
20

25



30

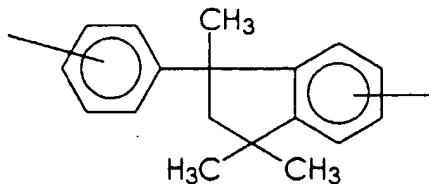
35



wherein w is an integer of from 1 to about 20,

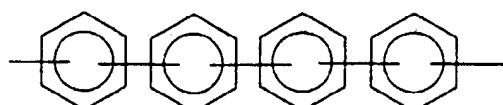
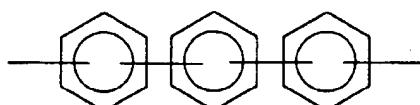
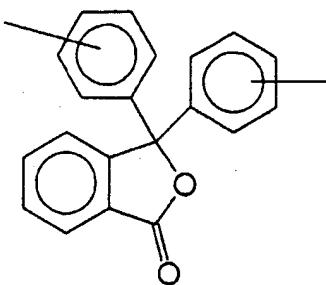
40

45



50

55



or mixtures thereof, and  $n$  is an integer representing the number of repeating monomer units, and (b) causing the polymer to become crosslinked or chain extended through the photosensitivity-imparting groups.

30

8. A process according to claim 7 wherein crosslinking or chain extension is effected by either (i) heating the polymer to a temperature sufficient to enable the photosensitivity-imparting groups to form crosslinks or chain extensions in the polymer; or (ii) exposing the polymer to actinic radiation such that the polymer in exposed areas becomes crosslinked or chain extended.

35

9. A process for forming a normal inkjet printhead comprising the steps of:

40

(a) depositing a layer (18) comprising a polymer according to any of claims 1 to 6 onto a lower substrate (28) in which one surface thereof has an array of heating elements (34) and addressing electrodes (33) having terminal ends (32) formed thereon;

45

(b) exposing the layer (18) to actinic radiation in an imagewise pattern such that the polymer in exposed areas becomes crosslinked or chain extended and the polymer in unexposed areas does not become crosslinked or chain extended, wherein the unexposed areas correspond to areas of the lower substrate (28) having thereon the heating elements (34) and the terminal ends (32) of the addressing electrodes (33);

(c) removing the polymer from the unexposed areas, thereby forming recesses in the layer (18), said recesses exposing the heating elements (34) and the terminal ends (32) of the addressing electrodes (33);

50

(d) providing an upper substrate (31) with a set of parallel grooves (20) for subsequent use as ink channels and a recess (24) for subsequent use as a manifold, the grooves (20) being open at one end for serving as droplet emitting nozzles; and

(e) aligning, mating, and bonding the upper (31) and lower (28) substrates together to form a printhead (10) with the grooves (20) in the upper substrate (31) being aligned with the heating elements (34) in the lower substrate (28) to form droplet emitting nozzles, thereby forming a thermal ink jet printhead.

55

10. An ink jet printhead (10) which comprises (i) an upper substrate (31) with a set of parallel grooves (20) for subsequent use as ink channels and a recess (24) for subsequent use as a manifold, the grooves (20) being open at one end for serving as droplet emitting nozzles, (ii) a lower substrate (28) in which one surface thereof has an array of heating elements (34) and addressing electrodes (33) formed thereon, and (iii) a layer (18) deposited on the surface of the lower substrate (28) and over the heating elements (34) and addressing electrodes (33) and

**EP 0 827 027 A2**

patterned to form recesses therethrough to expose the heating elements and terminal ends (32) of the addressing electrodes (33), the upper (31) and lower (28) substrates being aligned, mated, and bonded together to form the printhead with the grooves (20) in the upper substrate (31) being aligned with the heating elements (34) in the lower substrate (28) to form droplet emitting nozzles, said layer (18) comprising a crosslinked or chain extended polymer according to any of claims 1 to 6.

5

10

15

20

25

30

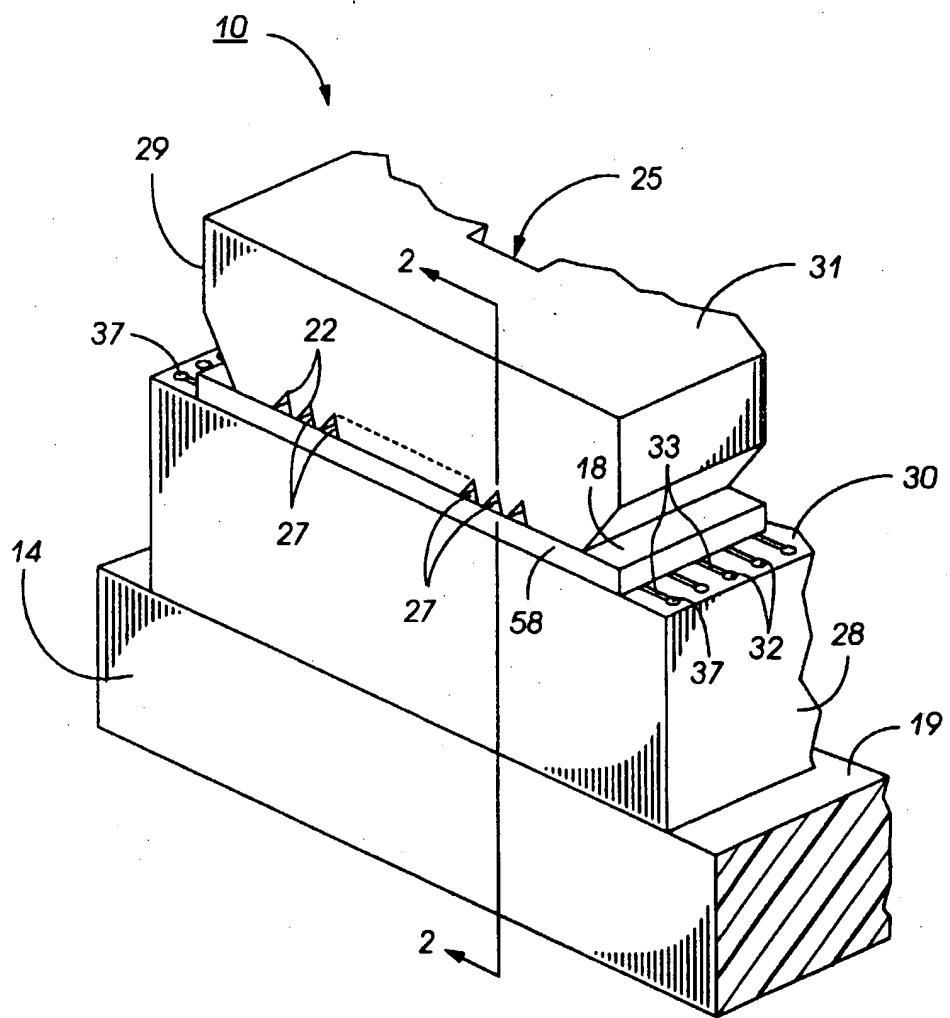
35

40

45

50

55



**FIG. 1**

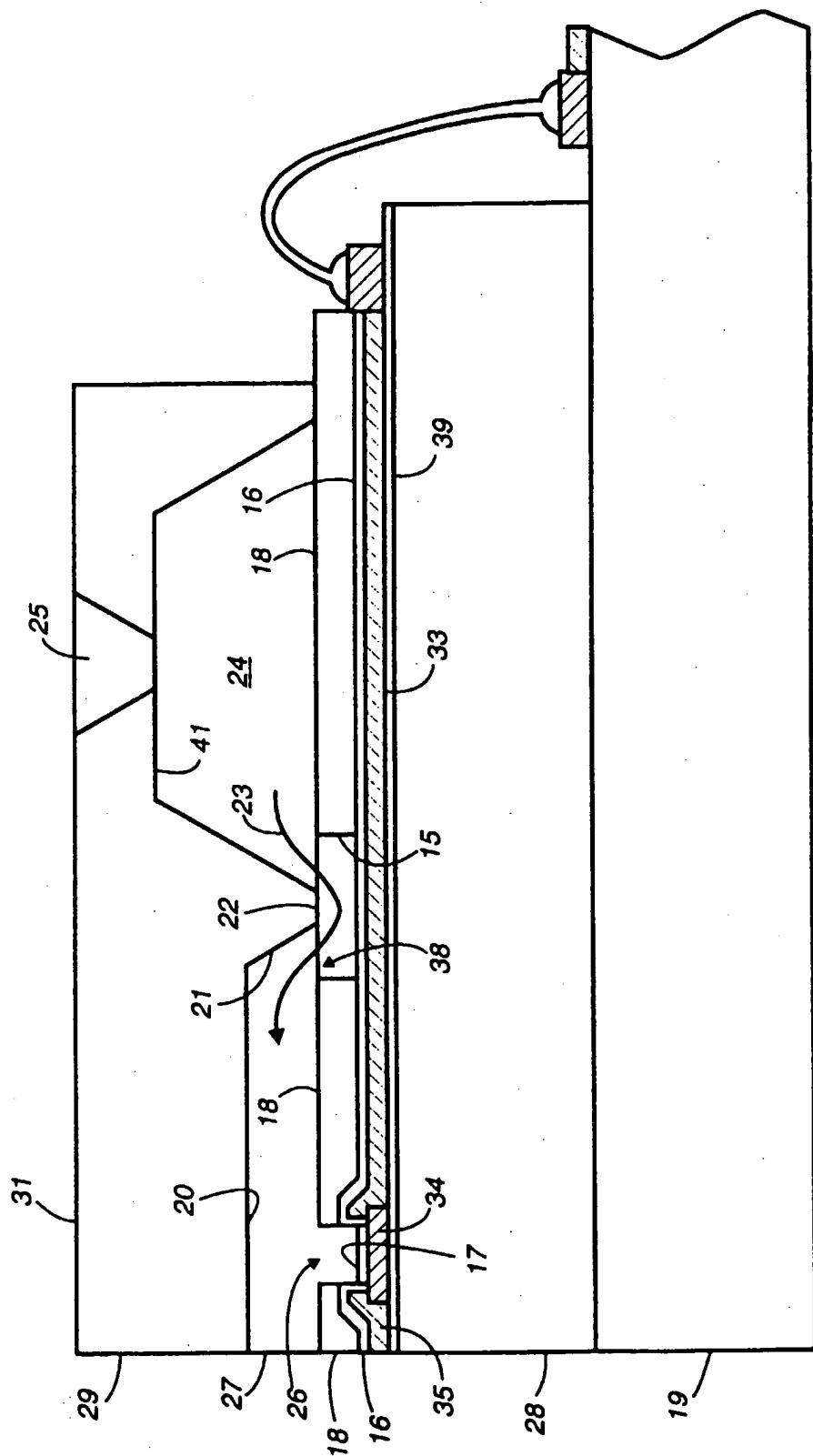


FIG. 2

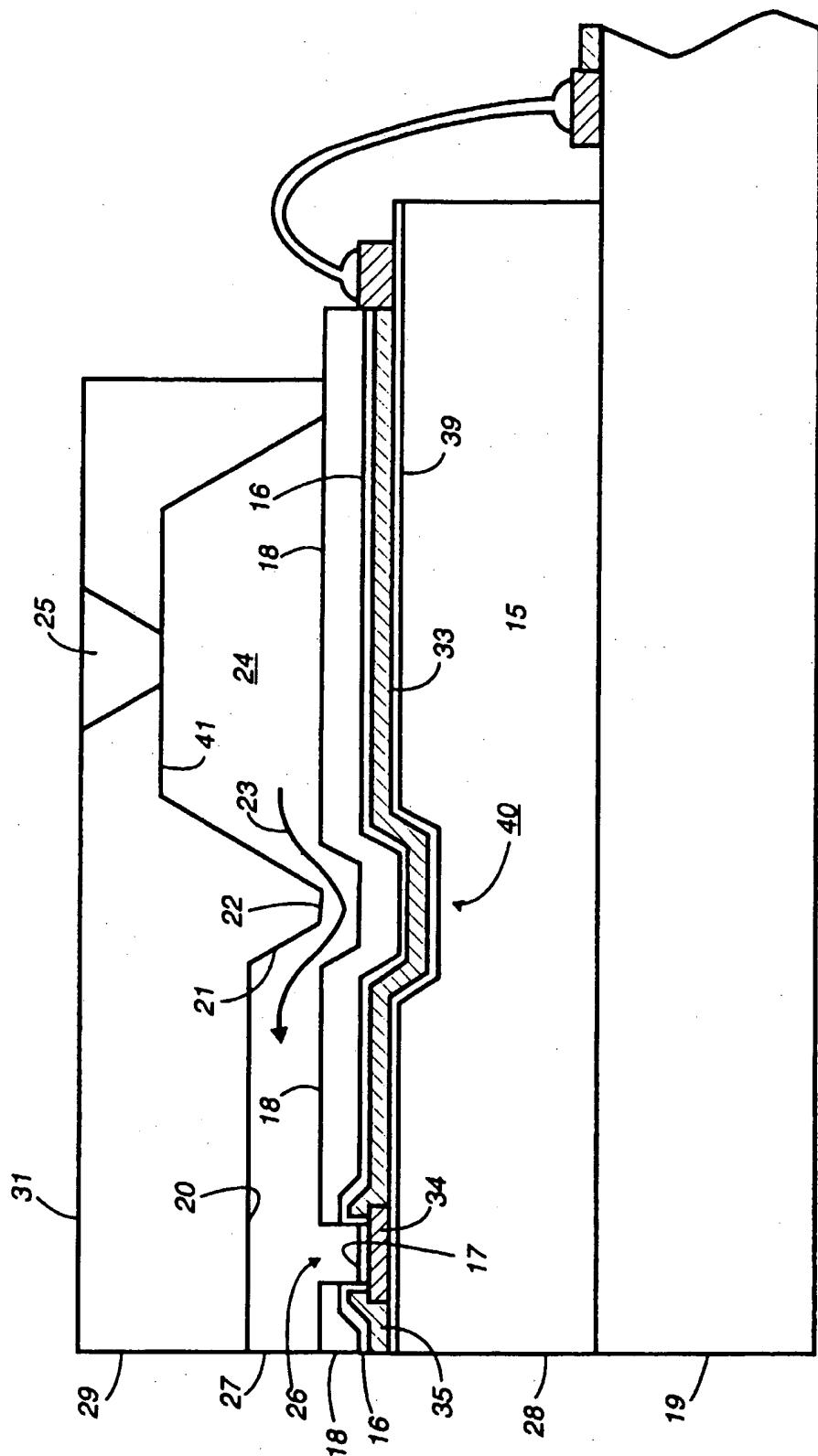


FIG. 3